Program: Horticulture Degree
Course title: Plant Biochemistry
Course credit: 5ects
Course code; HORT1042
Instructor's Name: Mitiku M.

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Evaluation ;Assessment 1 -3 50%**,** Final exam 50%(
Reference

Lehninger PRINCIPLES OF BIOCHEMISTRY, Fourth Edition by David L. Nelson (University of Wisconsin–Madison) and Michael M. Cox (University of Wisconsin–Madison)

Hans-Walter Heldt, 2005,.Plant Biochemistry, Third edition Elsevier Inc, California 92101-4495, USA

1. Introduction-2hrs

Learning objectives

- Define biochemistry

  - List the major macromolecules in cell
  - List and rank the element which are build cell
  - Define organic compounds and describe the different class of them
- How life going on living thing and what are the contribution of chemical on this process

What is chemistry?

1.1. Branches of Chemistry

- Inorganic Chemistry
  - the elements and their compounds (except carbon compounds)
- Organic Chemistry- the study of carbon compounds
  - substances containing carbon
- Physical Chemistry
  - scientific laws and quantitative relations governing the transformation of matter
- Analytical Chemistry
  - identity and composition of matter and the relative amounts that compose a particular substance
- Industrial Chemistry
  - chemical changes that take place in industrial processes
- Nuclear Chemistry
  - changes in the atomic nucleus
- Biochemistry
  - composition of substances that make up living things and the chemical processes that take place in plants and animals

1.2. Definition of biochemistry

- ☞ The study of
  - the chemical composition of living matter &
  - the chemical changes that occur in it during life processes.
- ☞ Explain both biological and chemical aspect of life.
- ☞ has become the basic language of all biologic sciences

1.3. The scope and objective of Biochemistry

- ➢ it scope is as wide as life itself
  - ⇨ whenever there is life, chemical processes are occurring.
  - ⇨ Biochemistry is concerned with the entire spectrum of life forms,
  - From viruses & bacteria to complex human beings
- ➢ Essential to all life sciences; e.g. Genetics, Immunology, Pharmacology, Physiology, Pathology, Microbiology, etc
- ❖ The major objective of Biochemistry
  - the complete understanding, at the molecular level, of all of the chemical processes associated with living cells
  - ➢ To achieve this objective, Biochemists have sought to:
    - ⇨ isolate the numerous molecules found in cells,
    - ⇨ determine their structures
    - ⇨ analyze how they function
- ❖ Many techniques have been used for these purposes;
  - ✓ Chromatography

- ✓ Electrophoresis
- ✓ Ultracentrifugation
- ✓ Specific sequencing methods

1.4. Chemical composition of cell

- ➢ The cell makes up all living organisms
- ➢ All the life process carried out inside cells
- The common life process for all organism
    1. Exchange matter and energy with their surroundings.
    2. Transform matter and energy into different forms.
    3. Respond to changes in their environment.
    4. Grow.
    5. Reproduction.

What are the chemical composition of cell?

- ☞ By ***elements***, a cell is composed of: 60% H, 25% O, 10% C, and 5% N, P, and S
- ☞ By **molecule** Cells are mostly water. The rest the present is ***macromolecules*** like:
- Polysaccharides, Lipids, Protein and Nucleic acid (DNA, RNA)

- ➢ All of life changes are due to large organic compounds called **macromolecules.**
- ➢ **Macromolecule** -large organic compounds
- is a combination of many smaller similar molecules polymerized into a chain structure.
- All of life changes are due to these molecules
- Build Cells and other macromolecules control the formation of these macromolecules.

1.5. Organic compounds

All life is made up of organic compounds

Organic compounds

- ⇨ Chemistry of the compounds present in living organisms
- ⇨ They all contain carbon
- ⇨ Four major classes of organic compounds are
    - Carbohydrates
    - Lipids
    - Proteins
    - Nucleic acids

Read an articles or books and come up with good understanding about organic compound classification, there major characters and occurrence.

Hydrocarbon

- the simplest of the organic compounds
- Contain only carbon (C) and hydrogen. (H)
    - The carbon to carbon can be single(A), double(B), or triple bonds(C).
    - The bonds are always nonpolar
- **Classified as** (*Alkanes(*C_nH_{2n+2}), Alkenes(C_nH_{2n}*)*, Alkynes(C_nH_{2n-2}

Derivatives of hydrocarbons

- Are formed when one or more hydrogen atoms is replaced by an element or a group of elements other than hydrogen.
- Are organic compounds that contain atoms other than C and H.

Functional Group

- Any atom, group of atoms, or organization of bonds that determine specific properties of a molecule
- the reactive part of the molecule.
  - ✓ Due to the functional group's presence, certain predictable properties ensue.
  - ✓ Example -phosphate group
    - The double bond in alkenes & triple bond in alkynes.
    - Cl atom, F atom, –OH group, methyl (CH_3 –) group.
    - Flavin (from Latin flavus, "yellow") is the common name for a group of organic compounds based on pteridine, formed by the tricyclic ...

Table; Macromolecules and their function groups

Organic cpd	Building block	Function group	Metabolism
Protein	Amino acids	Amino(R—NH_2) and carboxyl(–COOH)group.	Translation
Polysaccharids	Monosaccharide	2 or more hydroxyl group(—OH)	
Nucleic acid (DNA, RNA)	Deoxyribonucleotides		Replication/ transcription
Lipid	Faty acid, glycerol		

1.6. Molecules of life are break down and synthesized by living cells

Molecules of life are synthesized by living cells in the process of Metabolism

Processes of Metabolism

- All chemical reactions in the body constitutes metabolism
- Metabolism provides for the capture, storage and release of energy
- Cells use energy to grow and maintain themselves
- Enzyme-driven reactions build, rearrange, and split organic molecules

- Metabolism is the sum of all reactions
    - Through catabolism cells gain energy (break down of complex molecules)
    - Anabolism uses energy (synthesis of new molecules)

Life Functions or Processes

1. **Nutrition**: the obtaining & processing of materials by an organism for its use
    (a) ***ingestion*** *– food intake by an organism*
    (b) ***digestion*** *– breakdown of complex foods to simpler foods by an organism*
2. **Transportation** : [Circulation] distribution of materials within an organism
3. **Respiration:** process used by an organism to release energy from their food.
    (a) {Ex. Oxygen + glucose yields carbon dioxide + water+ ENERGY]
    (b) *This energy is needed to maintain life.*
4. **Synthesis** : combining simpler chemical substances to form more complex ones.
   Example- *Starches from simple sugars]*

5. **Excretion** : the removal of cellular wastes products
6. **Regulation** : (coordination) the control of various activities of an organism.
7. **Growth**: increase in living matter by increasing cell size or cell number
8. **Reproduction:** ability of organisms to form more of its own kind
    i. *(*not needed for an organism's survival but necessary for the survival of the species)*
9. **Immunity:** the ability of an organism to resist disease causing organisms and to fight invaders

- **Metabolism:** the sum total of all life processes needed to sustain life
- **Homeostasis** : the maintenance of internal stable environment by an organism (a steady state)
  ~ A disruption in any organism's system will result in a corresponding disruption of ***homeostasis***

Building Organic Compounds

- Cells form complex organic molecules
    - Simple sugars → carbohydrates
    - Fatty acids → lipids
    - Amino acids → proteins
    - Nucleotides → nucleic acids
- Dehydration synthesis combines monomers to form polymers

Overview of plant chemistry

- ☞ Plant material is a combination of cellulose (about 60%), lignin (about 30%), and other organic materials (about 10%).
- ☞ Cellulose is the structural material in plants (fibers)
- ☞ Lignin is the glue that holds the cellulose together
- ☞ Both start with simple sugars (glucose) made in Photosynthesis

Distinctive components of the aroma of some fruits and vegetables

Product	Compound	Product	Compound
Apple ripe	Ethyl 2-methylybutyrate	**Orange**	Valencene
Apple green	Hexanal, 2-hexanla	**Raspberry**	1-(Hydroxyphenyl)-3-butanone
Banana green	2-hexanal	**Cucumber**	2,6-Nondienal
Banana ripe	Eugenol	**Cabbage raw**	Allyl Isothiocynate
Banana overripe	Isopentanol	**Cabbage cooked**	Dimethyl disulphide
Grape fruit	Nootakatone	**Mushroom**	1-Octen-3-ol, lenthionine
Lemon	Citral	**Potato**	2-methoxy-3-ethyl pyrazine, 2-5 dimethyl pyrazine
Oinions	Ally propyl	**Radish**	4-methylthio-trans-3-butenylsothiocynate

2. Water, pH and Buffer-4hrs

2.1. General consideration for Water

- ☞ water is the **predominant chemical** component of living organisms
- ☞ it is the most important constituent of the body
- ⇨ Water is the solvent in aqueous solutions,
- ⇨ **Solution** -is a uniform mixture of two or more substances
- ⇨ **Solvent-** is the medium in which molecules of solute are dispersed

Water is universal Solvent

- The solvent of Life!
- an ideal biologic solvent for:
  - Polar solutes, with which it forms hydrogen bonds
  - Charged solutes, with which it interacts electrostatically
- Most vegetables and fruits = >80 g water/100 g produce
  - Cucumber, lettuce, melons = > 95 g water

- Starch tubers, seeds, yam, cassava, corn = less water but > 50 g
- The water content of the produce depends on
  - Available water at harvest
  - Diurnal variation in Temperature and RH

Therefore, for most harvesting should be at maximum possible water content b/c it results in crisp texture, esp. in leafy veges.

What is the difference between (1)polar and nonpolar molecules? (2)Hydrophobic and hydrophilic? Which molecules dissolve in water, polar or nonpolar? Why it dissolve?

Polar biomolecules dissolve readily in water because they can replace water-water interactions with more energetically favorable water-solute interactions. In contrast, nonpolar biomolecules interfere with water-water interactions but are unable to form water-solute interactions— consequently, nonpolar molecules are poorly soluble in water. In aqueous solutions, nonpolar molecules tend to cluster together. Non-polar compounds are hydrophobic and not easily dissolved in water.

2.2. Bonds and molecular structure

Structure of the water molecule

Water molecule is:

- ➢ an irregular, slightly skewed tetrahedron

The H—O—H bond angle is 105°:

- ➢ Slightly less than the 109.5^o of a perfect tetrahedron
- ➢ b/c of crowding by the nonbonding orbitals of the oxygen atom

Water is a dipole; a molecule with electrical charge distributed asymmetrically about its structure

- The strongly electronegative oxygen atom pulls electrons away from the hydrogen nuclei, leaving them with a partial positive charge,
- its two unshared electron pairs constitute a region of local negative charge

Bond in water

- ☞ Bonds Stabilize Biologic Molecules (covalent and non-covalent bond)
- ☞ **There are 4 Covalent bond** (unequal sharing of electron)
  Hydrogen bonds, ionic, hydrophobic, and van der Waals interactions

- lesser magnitude compare to noncovalent bond, make significant contributions to the structure, stability, and functional competence of macromolecules in living cells
- These forces, which can be either attractive or repulsive, involve interactions both within the biomolecule and between it and the water that forms the principal component of the surrounding environment
- are Individually weak, but collectively they have a very significant influence on the three-dimensional structures of proteins, nucleic acids, polysaccharides, and membrane lipids

1. Hydrogen bond

- Formed by interact with an **unshared electron pair** on another oxygen or nitrogen atom

- favors the self-association of water molecules into ordered arrays
- enables water to dissolve many organic biomolecules
- Gives water its unusual properties
    - provide the cohesive forces that make water a liquid at room temperature

2. Electrostatic Interactions

- Interactions b/n **oppositely charged** groups within or b/n biomolecules
- termed Salt bridges
- are comparable in strength to hydrogen bonds but act over larger distances.
- help for **shape** of biomolecular structure
- often facilitate the binding of charged molecules & ions to proteins and nucleic acids

3. Hydrophobic interaction

- Tendency of **nonpolar molecules** to self-associate in an aqueous environment

4. Van der Waals Interactions

- Weak Interatomic Attractions, when two **uncharged atoms** are brought very close together;
- their surrounding electron clouds influence each other
- the two dipoles weakly attract each other, bringing the two nuclei closer

2.3. Physical property

How the properties of water important for plant growth and development? Describe with example

Which property of water contribute for the following action of water

- ***When you put a droplet of water in paper, the water distributed in paper***
- ***When you put of water in minor, the water molecule make droplet by pulling together***
- ***How water reach from root of plant to shoot tip of plant via xylem tissue?***

Many properties of water are emergent properties due to **hydrogen bonding**.

- ☞ The polarity of water allows it to dissolve other polar molecules.

1. **Cohesion**= water attracted to other water molecules because of polar properties
    - ☞ water molecules move(river, fountain) too as a result of the adhesion
2. **Adhesion** = water attracted to other materials
    - ☞ Plant absorbed water from the soil due to adhesion
3. **Surface tension** = water is pulled together creating the smallest surface area possible
4. **Capillary Action**
    - It is the combine effect adhesive and cohesive properties of water.
    - Water move from root to shoot tip due to capillary action.
5. **High specific Heat Capacity**
    - ☞ In order to raise the temperature of water, the average molecular speed has to increase.
    - ☞ It **takes much more energy to raise the temperature of water** compared to other solvents because hydrogen bonds hold the water molecules together!
    - ☞ "The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius."
    - ☞ Water resists temperature changes by absorbing lots of heat

6. Density

- ➢ Water is less dense as a solid!
- ⇨ This is because the hydrogen bonds are stable in ice – each molecule of water is bound to four of its neighbors.
- Solid – water molecules are bonded together – space between fixed
- Liquid – water molecules are constantly bonding and rebonding – space is always changing

7. High heat of fusion

- a large drop in temperature is needed to convert liquid water to the solid state of ice

8. High thermal conductivity;

- facilitating heat dissipation from high energy-using areas such as the brain into the blood & the total body water pool

9. High heat of vaporization;

- ☞ as liquid water is converted to a gas and evaporates from the skin, we feel a cooling effect
- ☞ Water responds:
- • to the input of **heat**
- by decreasing the extent of hydrogen bonding
- • to cooling
- by increasing the bonding between water molecules

Unique physical properties of water

- Highly polar ← Dipolar nature of H_2O molecule
- Capable of forming hydrogen bonds with itself & solutes;
- Water has a higher melting point, boiling point, & heat of vaporization than most other common solvents

2.4. **Ionization of Water-splitting of water to H^+ & OH^-**

It is the ability of water to ionize, while slight, is of central importance for life

- ⇒ an intermolecular proton transfer that forms a H^+(a proton) & OH^-
- ⇒ the high ionic mobility of H^+ & OH^-
- ⇒ acid-base rxn's in aqueous solutions are generally exceptionally fast
- ⇒ can act both as an acid & as a base
- ⇒ giving the equilibrium: $H_2O \rightleftharpoons H^+ + OH^-$
- ⇒ reversible ionization is crucial to the role of water in cellular function

Measuring water ionization

- ☞ Can be measured by **its electrical conductivity**.
- ☞ Pure water carries electrical current as H^+ migrates toward the cathode & OH^- toward the anode. The movement of hydronium & hydroxide ions in the electric field is fast compared with that of other ions ← Na^+, K^+, & Cl^-.
- ☞ The ionization of water is expressed by **an equilibrium constant** ← K_{eq}

  Equilibrium constant ← K_{eq}

  $H_2O \rightleftharpoons H^+ + OH^-$

At 25 °C only about 2 of every 10^9 molecules in pure water are ionized at any instant. The equilibrium constant for the reversible ionization of water is

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]}$$

2.3. pH scale

- ☞ Designates the $[H^+]$ & $[OH^-]$ in any aqueous solution
- ☞ irange between 1.0 M H^+ and 10^{-14} M H^+
- ☞ The term pH is defined by the expression:

$$pH = \log \frac{1}{[H^+]} = -\log [H^+]$$

What the symbol p and H stand for?

- ☞ The symbol p denotes "negative logarithm of"
- ☞ The pH scale is logarithmic, not arithmetic
- ☞ To say that two solutions differ in pH by 1 pH unit means that one solution has ten times the H^+ concentration of the other but it does not tell us the absolute magnitude of the difference the pH of some common aqueous fluids A cola drink (pH 3.0) or red wine (pH 3.7) has $[H^+]$ H 10,000 times that of blood (pH 7.4)

Relationship between $[H^+]$ and $[OH^-]$

- ➢ In most aqueous solutions, $[H_3O^+]$ and $[OH^-]$ are not equal
- ➢ What happens to $[OH^-]$ when $[H_3O^+]$ is increased? Decreased?
  Since $[H_3O^+]\,[OH^-] = 1.0 \times 10^{-14} = K_w$ at 25 ^{0}C
  Increasing $[H_3O^+]$, $[OH^-]$ must decrease so their product equals 1.0×10^{-14}

Thus, when $[H_3O^+]$ is very high, $[OH^-]$ is very low, and vice versa

- ➢ In acidic solution, $[H_3O^+] > [OH^-]$
- ➢ In neutral solution, $[H_3O^+] = [OH^-]$
- ➢ In basic solution, $[H_3O^+] < [OH^-]$

Measurement of pH

How and why we measurement pH of a solution?

Measuring the pH of an aqueous solution can be

1. Indicator dyes;

- including: litmus, phenolphthalein, & phenol red
- undergo color changes as a proton dissociates from the dye molecule a

2. Glass electrode ← pH meter

- selectively sensitive to $[H^+]$ but insensitive to Na^+, K^+

pH is a measure of the concentration of hydrogen ions solution (Neutral, Acidic and Basic)

- Acids release hydrogen ions into solution
- Bases remove hydrogen ions from solution
  - Strong acids and strong bases ionize completely
  - Weak acids and weak bases do not ionize

Measures relative concentration of hydrogen ions

- pH 7 = neutral
- pH below 7 = acidic

- pH above 7 = basic
- Buffers - chemicals that control pH changes

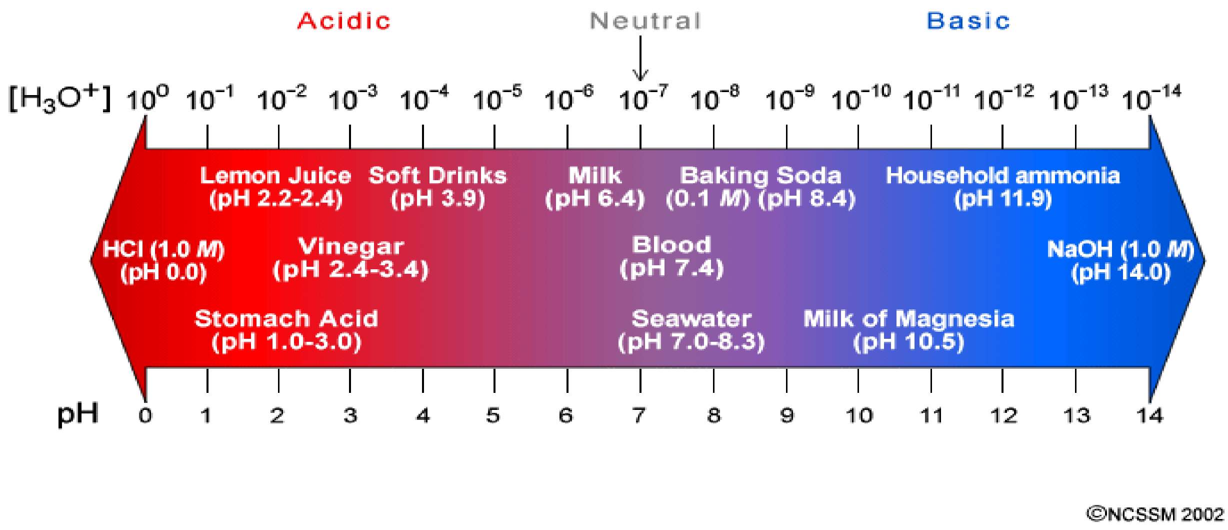
Measurement of pH one of the most important & frequently used procedures in biochemistry.

- ☞ The pH affects the structure & activity of biological macromolecules, for e.g.
- ☞ the catalytic activity of enzymes is strongly dependent on pH
- ☞ the rate physiological process affected by pH

Strength compared using pH scale

- ▪ Ranges from 0 – 14-Logarithmic Scale (gets 10x bigger/smaller)
- – Acid – donates H+ when added to aqueous solutions (Ranges from pH 0-6.9)
- – Base – breaks up into hydroxide (OH-) ions and another compound when placed in an aqueous solution (Ranges from pH 7.1 – 14)
- – Distilled water is pH 7.0 or neutral. Why?

H_2O H+ + OH-



2.5. Buffers

- ❖ It is a solution containing a weak acid and the salt of its conjugate base (or a weak base and the salt of its conjugate acid) which resist changes to its pH.
- ❖ **Resists changes in pH** by reacting with any added H^+ or OH^-, preventing their accumulation. How?
  - ⇨ Buffers remove or replace hydrogen ions in solution
  - ⇨ Buffer systems maintain the pH of body fluids

Any added H+ reacts with the base A^-:

H^+ (aq) + A^- (aq) -> HA(aq) (since A^- has a strong affinity for H+)

Any added OH^- reacts with the weak acid HA:

OH^- (aq) + HA (aq) -> H_2O + A^-(aq) (since OH^- can steal H^+ from A^-)

- ⇨ Buffers accept hydrogen ions from the solution when they are in excess and donate hydrogen ions when they have been depleted.

Biological buffers

The major buffer systems in the body are:

– Bicarbonate–carbonic acid buffer system, which operates principally in extracellular fluid
– Hemoglobin buffer system in red blood cells
– Phosphate buffer system in all types of cells
– Protein buffer system of cells and plasma

3. Carbohydrates-the dominant energy source of a cell-3 ECTS

3.1. General information about carbohydrates

Carbohydrate

- Poly-hydroxy **aldehydes or ketones**, or their derivative.
- Many, but not all, carbohydrates have the empirical formula $(CH_2O)_n$
    - o some also contain N, P, or S
- are the most abundant biomolecules on earth

Carbohydrates have Important Biological Roles:

- source Energy
- Structural and protective elements
- ✓ connective tissues of animals
- ✓ cell walls of bacteria & plants
- Lubricate skeletal joints
- Recognition & adhesion b/n cells
- ▪ Glycoconjugates
- act as signals that determine the intracellular location or metabolic fate of these hybrid
- Structural components of nucleic acids
- Metabolic precursors of all other biomolecules

3.2. Classification of Carbohydrates

There are three major classes of carbohydrates:

1. **Monosaccharides**: consist of a single polyhydroxy aldehyde or ketone unit
2. **Oligosaccharides**: a few monosaccharides covalently linked (2-20)
   ✓ Disaccharides - 2 monosaccharides covalently linked
3. **Polysaccharides**: polymers consisting of chains of monosaccharide or disaccharide units (>20)

3.2.1. Monosaccharaides

- ☞ The simplest of the carbohydrates:
- ☞ are either aldehydes or ketones with two or more -OH groups
- ☞ are colorless & crystalline solids;
- ☞ freely soluble in water but insoluble in nonpolar solvents
- ☞ most have a sweet taste

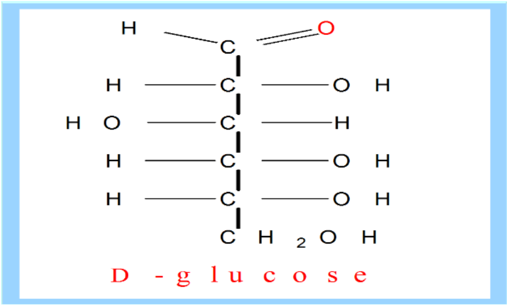
  monosaccharides of more than four carbons tend to have Cyclic structures

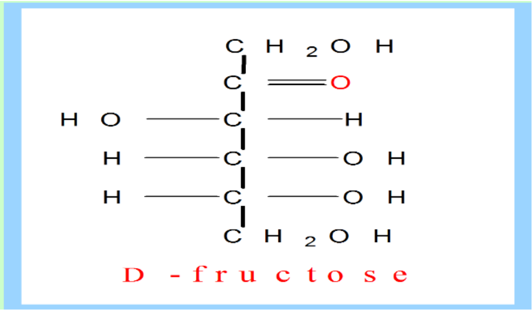
Aldehyde

- an group the monosaccharide the **carbonyl group** is at an end of the carbon chain

Ketose

- the carbonyl group is at any other position (C-2) a **ketone group** the monosaccharide





Aldehyde ketone

Glucose (blood sugar) is an aldehyde, and fructose (fruit sugar) is a ketone. Both have a molecular formula of $C_6H_{12}O_6$

The simplest monosaccharides are the two 3-C trioses:

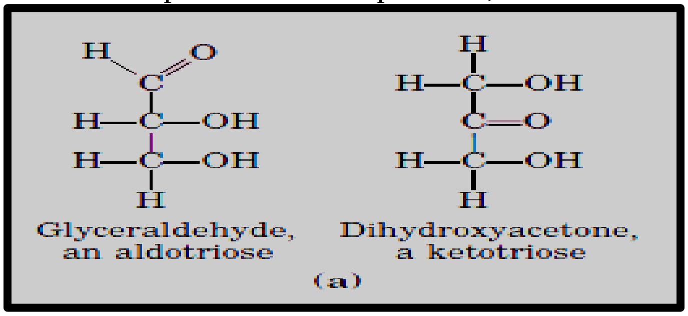
- ✓ Glyceraldehyde ← an aldotriose
- ✓ Dihydroxyacetone ← a ketotriose

Monosaccharides with 4, 5, 6, & 7-C atoms in their backbones are called, respectively,

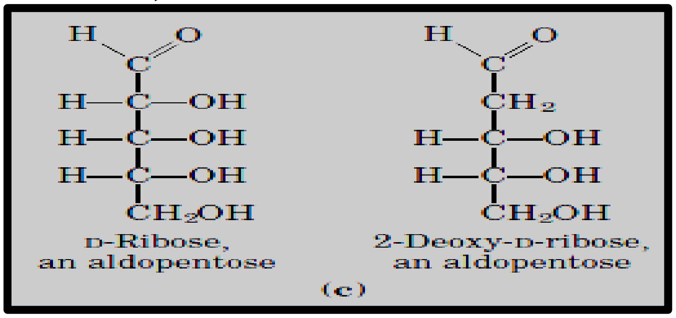
- ✓ Tetroses, pentoses, hexoses, & heptoses

There are aldoses & ketoses of each of these chain lengths:

- ✓ Aldotetroses & Ketotetroses
- ✓ Aldopentoses & Ketopentoses, & so on



Two trioses, an aldose and a ketose



The pentose components of nucleic acids:

- D-Ribose is a component of RNA &
- 2-deoxy-D-ribose is a component of DNA

Table-A. Pentoses of Physiologic Importance

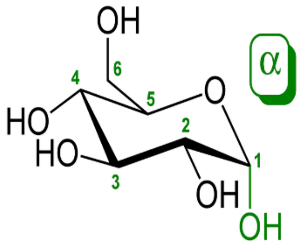
Sugar	Where found	Biochemical importance
D-ribose	Nucleic acids	Structural elements nucleic acids, wg. ATP, NAD, NADP, flovo-proteins, ribose phosphate are inter-mediates in pentose phosphate pathway
D-ribulose	Formed in metabolic processes	Ribulose phosphate is an intermediate in pentose phosphate pathway
D-Arabinose	Gum Arabic, plum and cherry gums	Constituent of glycoproteins
D-xylose	Wood gums, proteoglycans, glycosaminoglycans	Constituent of glycoproteins
D-Lyxose	Heart muscle	A constituent of a lyxoflavin isolated from human heart muscle
L-xylulose	Intermediate in uronic acid pathway	

Table-B. Hexoses of Physiologic Importance

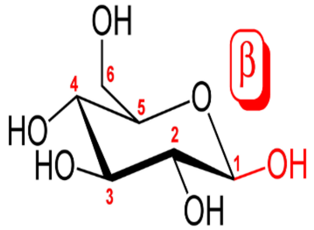
Sugar	Where found	Biochemical importance
D-Glucose	Fruits juices, hydrolysis of starch, cane, sugar, maltose and lactose	The sugar of the body
D-fructose	Fruits juices, honey, hydrolysis of cane sugar and of inulin,	Can be change to glucose in the liver and so used in the body
D-Galactose	Hydrolysis of lactose	Can be change to glucose in the liver and so used in the body
D-Mannose	Hydrolysis of plant mannans and gums	Constituent of glycoproteins

The a and b anomers of glucose.

- Note the position of the hydroxyl group (red or green) on the anomeric carbon relative to the CH2OH group bound to carbon 5:
- Either on the opposite sides (a)
- Or the same side (b).



(a)



(b)

Sugar Derivatives

Organisms contain a variety of sugar derivatives

There are a number of sugar derivatives in which

- ✓ a OH group in the parent compound is replaced with another substituent, or
- ✓ reduction of the carbonyl carbon of aldose to $–CH_2OH$
- ✓ a carbon atom is oxidized to a carboxyl group

  Sugars frequently contain

- ✓ Phosphate groups □ Amino groups
- ✓ Sulfate groups □ N-acetyl groups

3.2.2. Disaccharides

- ☞ Consist of 2 monosaccharides joined covalently by an O**-glycosidic bond**
- ☞ includes such as maltose, lactose, & sucrose

Sucrose:

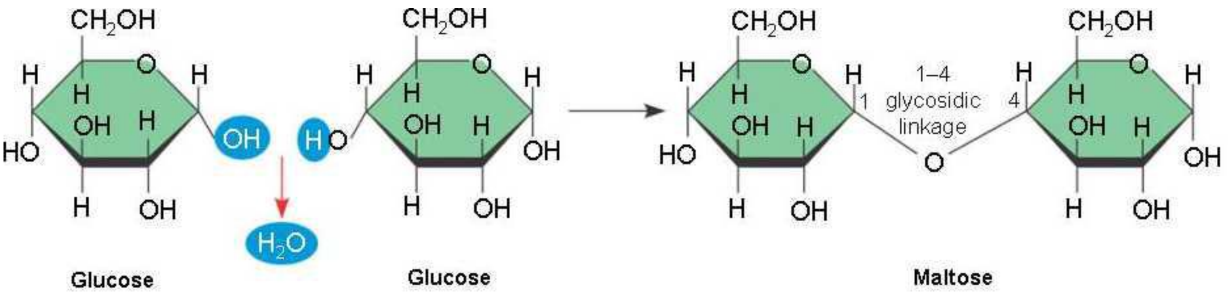
- common table sugar & a disaccharide of glucose & fructose
- a major intermediate product of photosynthesis

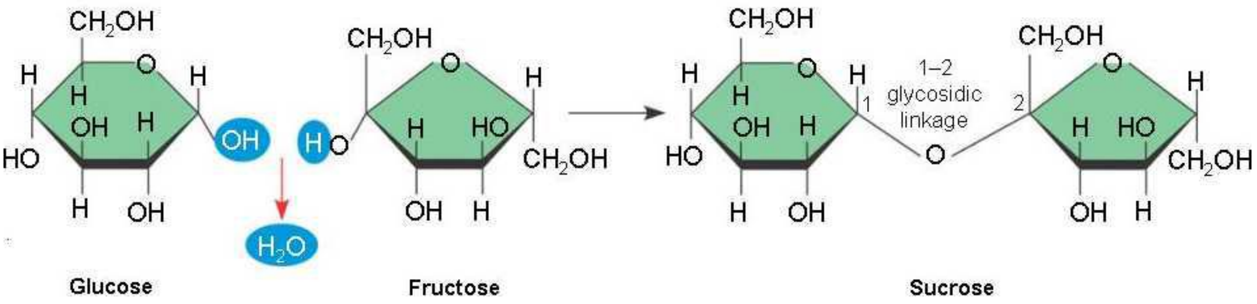
Maltose: 2G/c

- a cleavage product of starch (e.g., amylose)
- source; hagrolysis of starch germinating cereals and malts
- It is a reducing sugar

Lactose ←Gal (□1□4)Glc:

- milk sugar & composed of Gal & Glc;
- source; milk and many occur in urine during pregnancy
- Table-C. Disaccharides of Physiologic Importance





Reading assignment; Search in the internet and briefly describe the refining of Sucrose and Malting Process of maltose

3.2.3. Polysaccharides

- Structural polysaccharides are used to support plants
- Storage polysaccharides are used to store energy for later use by the plant

Differ from each other in the:

✓ *length of their chains*
✓ *the types of bonds linking the units*
✓ *Identity of their recurring monosaccharide units*
✓ *the degree of branching*

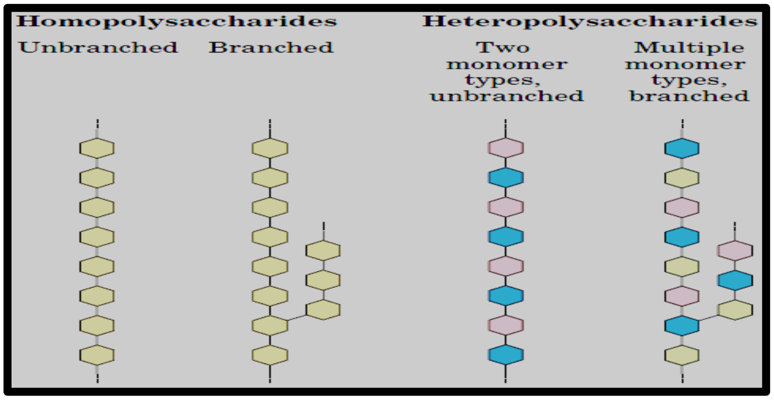
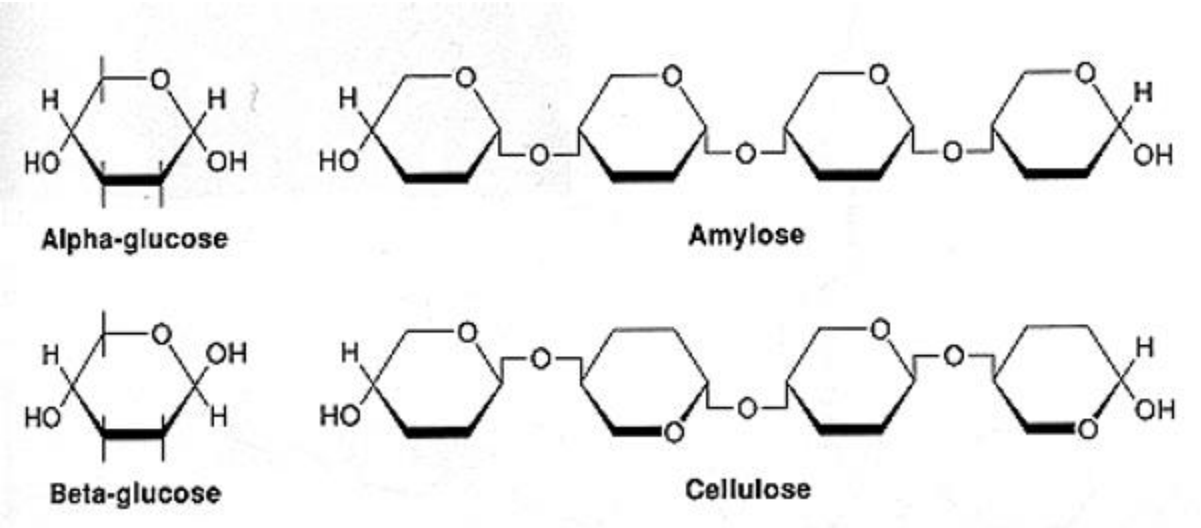


Figure - Homo- and Heteropolysaccharides

Structural Polysaccharides

- Includes celluloses, Pectins, and Hemicelluloses

Cellulose

- used in plant cell walls to maintain their structure
- The most common structural polysaccharide in plants
- It makes up 40 to 60% of the cell wall.
- It is also the most common polymer on earth
    - Via photosynthesis, over 100 billion metric tons of CO_2 and H_2O are converted into cellulose and other plant products.
- It is extremely strong due to its chemical organization.
- It is made of a long chain of beta-glucose molecules – 100 to 15,000 glucose molecules
- Cotton Boll – Pure Cellulose
- 

Gluey Polysaccharides

- ☞ **Pectins** are mainly polymers of galacturonic acid.
- ☞ **Hemicelluloses** are highly variable and are not related to cellulose.
    - Grass hemicelluloses are high in xylose, with small amounts of arabinose, galactose, and urionic acids.
    - pea family (Fabaceae) hemicelluloses are high in arabinose, galactose and urionic acid, but low in xylose.
- ☞ Some of the most interesting hemicelluloses are not actually used structurally, but rather are exuded from stems, leaves, roots, or fruits in a sticky mixture called a gum

What is the different between Pectins, Hemicelluloses and celluloses?

What is gum and its importance?

Storage Polysaccharides

- ☞ The most important storage polysaccharides are **amylose** and **amylopectin**.

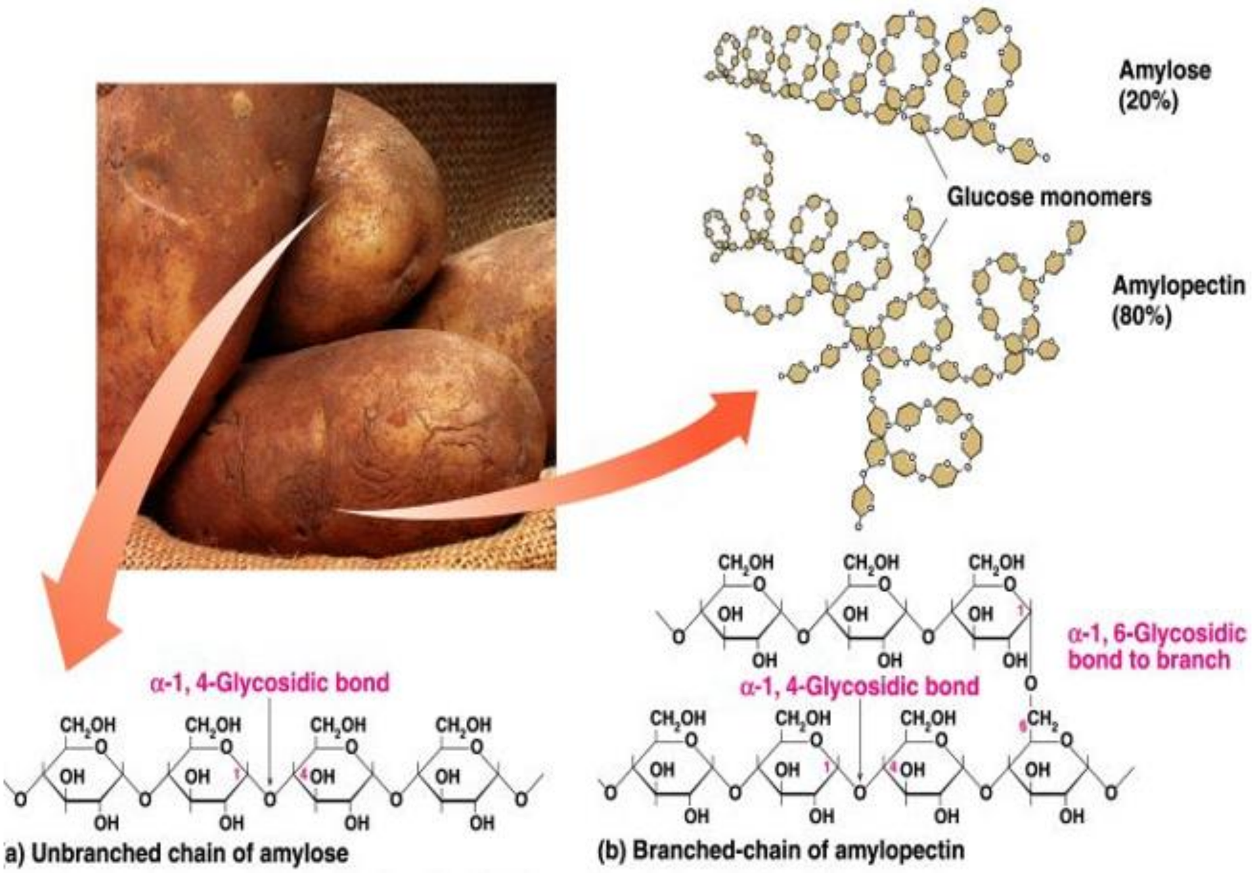
Amylose

- is a long chain of alpha-glucose, several hundred to several thousand molecules long.
- is an unbranched polymer (forms 〈-helix) of D-glucose molecules linked by 〈-1,4-glycosidic bonds

Amylopectin

- is more complex, often made up of 50,000 molecules

   - is like amylose, but has extensive branching, with the branches using 〈-1,6-glycosidic bonds.
- ☞ These two polymers are both used in making starch grains. Most starch grains are about 20% amylose and 80% amylopectin, but this varies with the plant species**.**
- ☞ **Starch** contains a mixture of amylose and amylopectin
- ☞ **Inulin** – another storage carbohydrate – long chain of fructose
- ☞ **Glycogen** is a storage carbohydrate used by animals.



Digestability

- The properties of alpha-glucose and beta-glucose affect their digestability. Alpha-glucose polymers don't form fibrils and thus are not as strong as cellulose from beta-glucose. Even more important, almost all organisms have alpha-amylase, a digestive enzyme that breaks down alpha-glucose bonds. So starches can be digested easily. Plants have alpha-amylase so they can harvest energy from starches in their seeds, roots, and tubers.
- Very few organisms have cellulases – just some fungi and bacteria, earthworms, and a few insects can digest cellulase.

Carbohyadete content of horiticultural crops

- Are most abundant next to water
- They range from simple sugars to complex ploymers, w/c contain many hundreds of monomeric units

- Carbohydrates can account for 2-40 g/100 g of produce tissue
  - Low levels in cucrbits e.g cucumber
  - High levels in starch accumilating veges, e.g. cassava

The main types of sugars in fruits and veges are:

- Sucrose, glucose, and fructose
- Glucose and fructose occur in all produce and are often present at similar levels
- Sucrose is only present in about 2/3 of produce
- Highest level of sugars are found in tropical and subtropical fruits, with grape being the only temperate fruit listed
- No vegetables are listed

Sugar content (g/100g fresh wt) of some fruits and vegetables

Produces	Glucose	Fructose	Sucrose
Apple	3	6	2
Banana	4	4	10
Beet root	<1	<1	8
Capsicum	2	2	0
Cherry	6	4	0
Grape	8	8	0
Onion	2	2	1
Orange	2	2	4
Pea	<1	<1	4
Peach	1	1	5
Pear	2	7	1
Pine apple	1	2	5
Tomato	1	1	0

Fruit & vegetables with the highest sugar levels

Produce	Total sugars	Glucose	Fructose	Sucrose
Banana	17	4	4	10
Jackfruit	16	4	4	8
Lichi	16	8	8	1

Persimmon	16	8	8	0
Rambutan	16	3	3	10
Grape	15	8	8	0
Custard apple	15	5	6	4
Pomegranate	14	8	6	0
Carambola	12	1	3	8
Mango	12	1	3	8

Ss

- Beet root contains the highest sugar among veges (8 g/100 g) with sucrose the only sugar present
- Much of the sensory appeal for fruits is due to sugar since sweetness is the universal innate human taste preference
- Produces such as cassava and yam commonly contain > 20g / 100 g as starch
- Starch from
  - **Plantain, cassava, yam, taro, Sweet potato and potato** provide the bulk of energy in the diet of subsistence group
- Cellulose, pectin substances and hemicelluloses are the main carbohydrate polymers that constitute fiber.
- Dietary fiber is not digested by humans b/c
  - Enzymes are not secreted that can break down ploymers to monomers that can be absorbed.
    - Starch – requires amylase
    - Cellulose- requires cellulase
    - Pectin- pectinase
    - Etc.
- Dietary fiber, though has no nutritional value
  - Avoids constipation
  - Avoids a raft of diseases, mostly affiliated to western countries (Diseases of affluence)

4. Protein

Learning Objectives

- ☞ After reading this chapter you should be able to:
- ☞ Classify proteins based on their biological value, axial ratio, function, & chemical composition.
- ☞ Identify the major types of bonds participating in the protein structure.
- ☞ Describe the elements of the primary, secondary, tertiary, & quaternary structure of proteins.

- ☞ Describe the function of proteins.

Topics to be discussed

- ☞ Overview of proteins
- ☞ Functions & Classification of proteins
- ☞ Structural organization of proteins
- ☞ Bonds stabilizing the protein structure
- ☞ Properties

➓Denaturation ➓Solubility ➓Precipitation

4.1. General outlines about proteins

- ☞ Organic compounds containing C, O, H & N
- - also they may contain ← S, P, non-protein organic groups & metal ions
- ☞ it polymer of amino acid
  - o Amino acid chains are linked by **peptide bonds** in condensation reactions.
    - **Dipeptides** have two amino acids bonded together.
    - **Tripeptides** have three amino acids bonded together.
    - **Polypeptides** have more than two amino acids bonded together.
- ☞ Amino acid sequences are all different, which allows for a wide variety of possible sequences.
- ☞
- ☞ The most abundant biological macromolecules
  - - occurring in all cells & all parts of cells
  - - Over 50 % of a cells dry weight is Protein
- ☞ exhibit enormous diversity of biological function
- ☞ are the most important final products of the information pathways
- ☞ molecular instruments through w/c genetic information is expressed

4.2. Amino Acids

- ☞ Organic acids that contain both an amino and carboxyl group
- ☞ Structural units of proteins
- ☞ Each AA has a central carbon, called the α-carbon; to w/c four different groups are attached(fig.1):
  - - **Carboxyle groups**(–COOH); proton donor acid by to get negative charges &
  - - **amino group** (–NH2); proton accepting base by to get positive charges
  - - **side chain**
  - - **H**
- ☞ Exception ← Proline
- • Have an unionizable imino (–NH–) group.

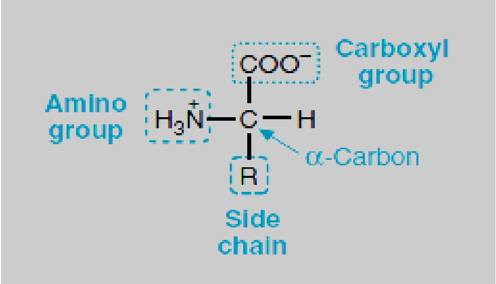


Figure 1. General structure of the amino acids found in proteins

Classification of AAs

- ❖ Although about 300 amino acids exist in cells,
  - ☞ only 22 of them are polymerizable into protein structure known as protein amino acids,
  - ☞ those that do not occur in proteins are called as non-protein amino acids
- ❖ Based upon whether the AAs can be synthesized in human body or not

1. **Indispensable or essential AAs**
   - ☞ not synthesizable in the body in adequate amounts.
   - ☞ Ten AAs are essential: Val, Ile, Thr, Trp, Arg, Leu, Lys, Met, Phe and His.
2. **Dispensable or non-essential AAs**
   - ☞ Synthesizable in the body and there is no diet dependency for them.

- ❖ **Arg &His are semi essential;**
  - ☞ the healthy adult human body synthesizes them
  - ☞ not enough in the Childhood growth period, sickness, convalescence and during pregnancy
- ❖ Some AAs become essential under certain conditions:
  - ☞ Tyr also turns essential upon dietary deficiency of Phe
  - ☞ Cys turns essential upon dietary deficiency of Met

Table1. the name and Abbreviations of amino acids

No	Name	abbreviations		No	Name	abbreviations	
		Three letters	One letter			Three letters	One letter
1	Alanine	Ala	A	11	Leucine	Leu	L
2	Arginine	Arg	R	12	Lysine	Lys	K
3	Asparagine	Asn	N	13	Methionine	Met	M
4	Aspartate	Asp	D	14	Phenylanine	Phe	F
5	Cysteine	Cys	C	15	Proline	Pro	P
6	Glutamate	Glu	E	16	Serine	Ser	S
7	Glutamine	Gln	Q	17	Threonine	Thr	T
8	Glycine	Gly	G	18	Tryptophan	Trp	w
9	Histidine	His	H	19	Tyrosine	Try	Y
10	Isoleucine	Ile	I	20	Valine	Val	V

Three letter abbreviations are generally used; one letter abbreviations are used mainly to list the amino acid sequence of long protein chains.

4.2. Function and classification of proteins

Function of proteins

- ➢ **Structural**: main structural component in bone, muscles, cytoskeleton & cell membrane, cell wall
  - Structural proteins make up 2 to 10% of the cell wall in plants. Expansins help increase the surface area of cell walls. Extensins help protect or repair damaged cell walls. The plant cell membrane is about 50% structural proteins.
  - Storage proteins are used mostly in seeds and are used as source of nutrition for the early development of seedlings. Storage proteins used in seeds vary considerably between

plant species. Corn produces a storage protein called ZEIN. Wheat produces a storage protein called GLIADIN

- **Nutrition**: provide the body with essential AAs, N & S
- **Catalytic**: almost all metabolic enzymes are proteins in nature
- **Endocrin**e: most of hormones and all receptors are protein in nature
- **Defense**; antibodies
- **Osmotic potential**; plasma proteins
- Blood clotting factors are proteins
- **Transport** Role: Hemoglobin

Classification

- About 26,000 to 40,000 genes in human genome coding for about 28,000 proteins.
- Proteins may be: simple monomeric or complex oligomeric with or without a conjugated non-proteinacious ligand.
- Different criteria for classification can be used; such as

1. Biological value
2. Axial ratio; The composition of protein
3. Solubility and Physical properties; Function

criteria for classification	**Classification**	**Description**	**Examples**
Biological/ nutritional value (digestibility and composition of AA)	High value	when they are easily digestible contain all the essential AAs in well balanced proportions	
	Low value	when they are deficient in one or more EAAs, or containing very little amount of one of them, or are indigestible	
Axial ratio(the ratio of their shortest to longest dimensions (L / W))	Fibrous	proteins with an axial ratio of ≥10 are fairly resistant & sturdy majority have structural function	Keratins in hairs, wool, skin, nails & cytoskeletons Myosin of the muscles
	Globular	the proteins with an axial ratio not over 3 are compact, roughly spherical molecules less stable than fibrous proteins =>more liable to denaturation	Enzymes, hormones , transport proteins, cymotrypsin, lgs, albumin, Hb, insulin
Their composition	Simple	Proteins composed of AAs only	Insulin, myosin, albumin
	Conjugated	Proteins carry certain non-AA prosthetic groups	
	Derived	All the proteins derived from either of the above two types	

Function		Defence	
		Respiration	
		Contractile	
		Signal transduction	
		structural	
		Enzymes	

4.3. Structural Organization of Proteins

- ➢ Function of monomeric or polymeric proteins is determined by
- ⇨ their sequence, structural conformation &
- ⇨ nature of interaction among its structural units, i.e., sequence-structure-function relationship.
- ➢ Four levels of organization of protein structure:
  1. Primary (sequence)
  2. Secondary (local folding)
  3. Tertiary(tertiary range folding)
  4. Quaternary(multimeric organization)

This complication gives the molecule its functional **domain** to explain its structure-function requirements that if changes due to mutation will give non-functional protein ➘disease

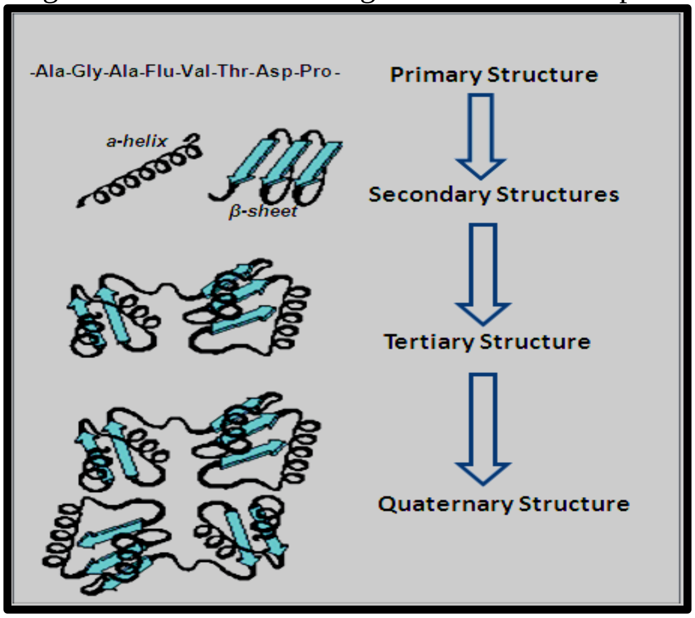


Fig-1 .Levels of structure in proteins

1. Primary Structure

- ☞ It is the **linear sequence of AAs** in the polypeptide chain
- ☞ Illustrating: the total number, chemical nature, & linear order of all of the AA residues in the polypeptide chain,
- ☞ Substitution of a single AA for another may reduce or abolish biologic activity of the protein with potentially serious consequences,
- e.g., **sickle cell anemia** where; Glu at position 6 of the ®-chains is replaced by a Val

2. Secondary Structure

- recurring, localized structures formed at a regions within polypeptide chains
- The two regular secondary structures called the 〈**-helix** & ®**-sheet** ➘ contains repeating elements formed by hydrogen bonding b/n atoms of the peptide bonds
- Other regions of the polypeptide chain form nonregular nonrepetitive secondary structures, such as **coils, loops, & turns**

Characteristics of α-Helix

- is most common secondary structure
- It is a rod-like structure with the peptide chain & **tightly coiled** about ¼ of all AA residues in polypeptides are found in α-helices

β-Pleated Sheets

- If the H-bonds are formed b/n peptide bonds in different chains, the chains become **arrayed parallel or antiparallel to one another** in what is commonly called a β-pleated sheet
- It is an extended structure as opposed to the coiled α-helix. It is pleated b/c the C-C bonds are tetrahedral & cannot exist in a planar configuration
- If the polypeptide chain runs in the same direction, it forms a parallel β-sheet but in the opposite direction, it forms an antiparallel structure

3. Tertiary Structure

- refers to the entire 3D conformation of a polypeptide
- It indicates, in 3D space, how secondary structural features ➘helices, sheets, bends, turns, & loops assemble to form **domains** how these domains relate spatially to one another

Domains

- **i**s the folded conformation of proteins that contain more than 200 residues consists of several smaller folded units
- it is a section of protein structure **sufficient to perform a particular chemical or physical task** such as binding of a substrate or other ligand

4. Quaternary Structure

- an **assembly of two or more separate peptide chains** that are held together by noncovalent or, in some cases, covalent interactions
- **multi subunit proteins/ Polymeric proteins**
  - ⇨ proteins larger than 50 kDa
  - ⇨ consist of more than one chain
  - ⇨ referred to as **dimeric, trimeric, or multimeric** (oligomeric) proteins
  - ⇨ are composed of different kinds of functional subunits, such as the regulatory & catalytic subunits
- The smallest unit is referred to as a **monomer or subunit**.
- **Polymeric proteins** could be:
  1. **homooligomeric**; several polypeptides of the same type
  2. **heterooligomeric**; several polypeptides each with different sequence,
- ☞ Greek letters (〈, ®, ©, etc) are
  - used to distinguish different subunits of a heterooligomeric protein,
  - subscripts indicate the number of each subunit type, e.g.

- 〈$_4$ designates a homotetrameric protein,
- &〈$_2$®$_2$© a protein with five subunits of three different types

- ☞ Oligomeric proteins are very common among enzymes e.g., carbonic anhydrase is composed of 27 polypeptides
- ☞ The structure of the dimeric protein, Cu,Zn-superoxide dismutase

Denatured of protein

- If a protein unfolds and loses its three-dimensional shape (denatures), it also loses its function
- Caused by shifts in pH or temperature, or exposure to detergent or salts or heavy metals
- Disrupts hydrogen bonds and other molecular interactions responsible for protein's shape

Protein in horticultural crops

- Fresh fruits and vegetables contain = 1g/100 g in fruits
- 2 g /100 g in vegetables
- Most abundant being in
  - Brassica veges, 3.5 g protein/100 g
  - Legumes, 5 g /100 g
- The protein is mostly functional as in the form of enzymes rather than storage organ
- Fresh fruits and vegetables are not important sources of protein

5. Enzyme

Learning Objectives

After reading this chapter you should be able to:

- ☞ Describe the characteristics of enzymatic rxn's
- ☞ Discuss the structure and composition of enzymes, including cofactors, and conditions that affect enzymatic rxn's.
- ☞ Describe the elements of enzyme structure that explain their substrate specificity & catalytic activity.
- ☞ Describe enzyme kinetics based on the Michaelis-Menten equation
- ☞ Describe regulatory mechanisms affecting enzymatic rxns
- ☞ Differentiate among the three types of enzyme inhibition

5.1. General information and importance

- Fundamental conditions for life:
- ✓ Self-replicate
- ✓ Catalyze chemical rxns; Efficiently, Selectively

Definition-

Enzymes are protein molecules that catalyze (enhance) biochemical rxns in the biological systems

- Produce by living cell
- The number and the types of reactions catalyzed by an enzyme are determined by the specificity of the enzyme.

General concept

- Almost all enzymes are composed of protein
  - ☞ Most proteins in living cells are enzymes.
  - ☞ Found in all tissues & fluids of the body
- Enzymes catalyze biochemical reactions.
- do not invent new rxn's; simply facilitate rxn

Practical importance

Study of enzymes have immense practical importance:

- ☞ Chemical industry
- ☞ Food processing & Agriculture
- ☞ Health
  - ✓ To study diseases; there may be; ❿a deficiency ❿even a total absence, or ❿excessive activity
- ☞ Medicine
  - ✓ Many drugs exert their biological effects; through interactions with enzymes

- ☞ Pure enzymes that maintain their activity when removed from plants are commercially important to us.
  - Papaya – Papain and Chymopapain
  - Pineapple – Bromelain

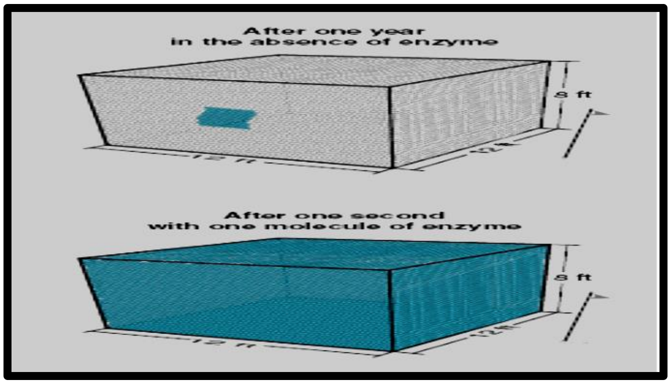
Source of enzymes

የደቂቅ ዘአካላት መገኛው (Microbial sources)	ኢንዛይም	የሚሰጠው የምርት አገልግሎት (Typical application)
Bacteria		
Bacillus subtilisin	Neutral protease	Brewing
Bacillus subtilisin	α- Amylase	Starch modification
Fungi		
Aspergillus niger	Pectinase	Fruit juice processing
Aspergillus niger	Amyloglucosidase	Starch processing
Rhizopus oryzae	Lipase	Lipid modification
Rhizomucor spp.	Acid protease	Cheese production
Trichoderma Longibrachiatum	Cellulase	Brewing
Yeast		
Sacharomyces cerevisiae	Inventase	Confectionery
Kluyreromyces cactis	Lactase	Dairy

Fundamental Properties of Enzymes

Enzymes in general provide:

- Speed
- Specificity
- Regulatory control



5.2. Components of enzymes

Chemical groups required for enzymes activity other than their amino acid residues are;

- ❖ **Cofactor**: non protein component, includes
  - ● **metal ions** (inorganic) -activators
  - ● **Coenzyme** (organic)
    - ✓ act as transient carriers of specific functional groups
    - ✓ most are derived from water soluble **vitamins**
- ● Some enzymes require both a coenzyme & metal ions for activity
- ● It may be attached either loosely or tightly to the enzyme
  - **Prosthetic group**-if cofactors attached tightly
- ❖ **Apoenzyme** –protein component
- ❖ **Holoenzyme**-cofactor and apoenzyme

5.2. Chemical reaction by Enzyme

Active site

- ❖ A site on enzyme where Substrates bind on
- ✓ **complementary** to a portion of the substrate
- ❖ simultaneously aligns those portions of the substrate that will undergo change with the functional groups
- ❖ help for
- ☞ shields substrates ← from solvent
- ☞ facilitates catalysis
- ❖ Active site also binds & orients cofactors

Binding Interaction b/n E & S

Two Aspects:

1. **Lock-and-key Model**: *Emil Fischer*, Late in the 19th century
   - ● describe highly specific fit b/n E & their S
   - ● accounted for the exquisite specificity of ES interactions,

- ✓ The implied **rigidity** of the enzyme's active site
- ✓ failed to account for the dynamic changes that accompany catalysis.

2. **"Induced Fit" Model**: *Daniel Koshland's*
   - ❖ complementarity b/n S & binding site →
   - ❖ undergo a **conformational change** → "induced fit"
   - ❖ repositions the side chains of the amino acids in the active site
   - ✓ increases the number of binding interactions

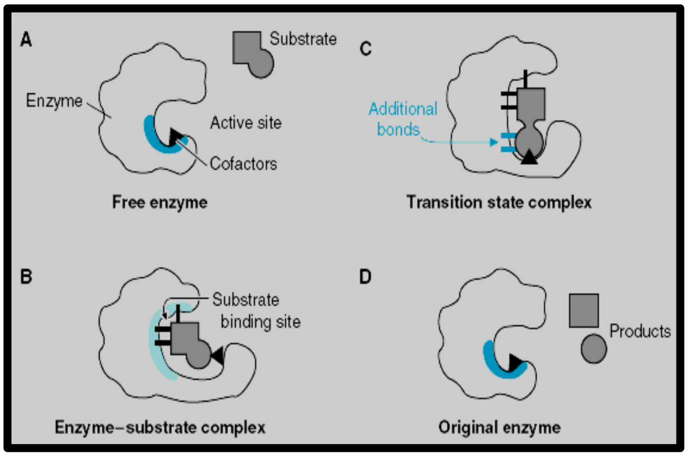


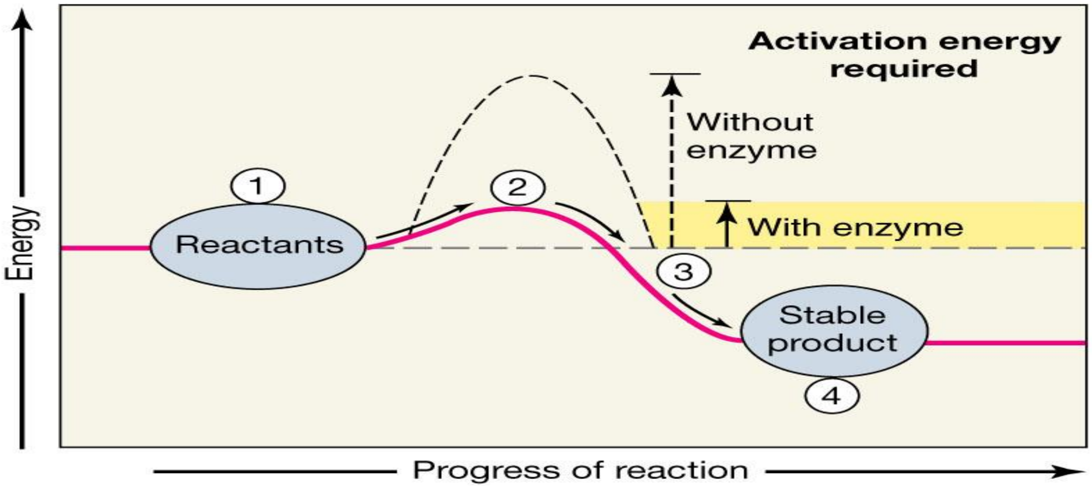
Fig. 2 Rxn in the Enzyme Active Catalytic Site. NB 10

Enzyme-Catalyzed Rxn

How enzyme enhance chemical reaction

Enzymes, energy and chemical reactions

- Activation energy is the amount of energy needed to begin a reaction
- Enzymes are catalysts
  - Reduce energy of activation without being permanently changed or used up
  - Promote chemical reactions



Three basic steps:

1. Binding of substrate: E + S ↓ ES

2. Conversion of bound substrate to bound product: ES ↓ EP
3. Release of product : EP ↓ E + P

   E + S ↓ ES ↓ EP ↓ E + P

   To catalyze a chemical rxn ➘ the enzyme forms Enzyme-substrate complex ➘ *Charles Adolphe Wurtz in 1880*- central to the action of enzymes

Enzyme participates in the:

- making & breaking of bonds, ➘ for product formation
- releases the products, &
- returns to its original state

The Michaelis-Menten(MM) Model:

☞ a simple model of an enzymatic rxn accounts for the kinetic properties of many enzymes

☞ It is based on the assumptions that: E, S, & ES are in ***rapid equilibrium*** with one another

- so that a steady conc. of ES is **rapidly** achieved
- The conversion of ES into E + P is a **rate-limiting**, irreversible step

Modern derivation of the MM-equation:

- includes steady-state assumption derivation starts with the 2 basic steps of the formation & breakdown of ES;

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P$$

- early in the rxn, the [P] is negligible, & the simplifying assumption that the reverse rxn, P❼ES (k_{-2}) can be ignored.
- the overall rxn then reduces to;

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$$

Factors Affecting Rxn Velocity

Multiple Factors Affect ← rxn velocity (rates):

Kinetic theory *(or, collision theory)* - of chemical kinetics states that:

- For two molecules to react they must;
  - approach within bond-forming distance of one another, or "**collide**"
  - possess sufficient **kinetic energy** to overcome the energy barrier for reaching the transition state
- It therefore follows that;
  - anything that ←es the frequency or energy of collision b/n substrates will ←es the rate of the rxn in w/c they participate

Factors enzyme activities

Temperature	✛pH & Buffer	✛Ionic strength
Substrate Conc.	✛Enzyme Conc.	

5.3. Enzyme Inhibition

Inhibitors:

- ☞ compounds that decrease the rate of an enzymatic rxn
- ☞ Classified based upon:
- their site of action on the enzyme,
- whether or not they chemically modify the enzyme, or
- the kinetic parameters they influence

Two broad classes of inhibitors:

1. **Reversible inhibitors**
   - the enzyme became active after removal of the inhibitor
   - I. **Competitive inhibitor**
     - ✓ typically resemble S, substrate analogs
     - ✓ occupies the active site
   - II. **Uncompetitive inhibitor**
     - ✓ Binds only to the ES complex
     - ✓ Not to the free enzyme
     - ✓ Not to the active site
   - III. **Noncompetitive inhibitor**
     - o also binds at a site distinct from; the substrate active site, but it binds to either E or ES
     - o Its binding does not affect binding of S
     - o E & EI possess identical affinity for S
2. **Irreversible Inhibitors (IIs)**:
   - ❖ bind covalently with or destroy a functional group on an enzyme
   - ❖ form a particularly stable noncovalent association
     - Act irreversibly by chemically modifying the enzyme
     - These covalent changes are relatively stable,
   - ◆ an enzyme that has been “poisoned” by an irreversible inhibitor
   - • remains inhibited even after removal of the remaining inhibitor from the surrounding medium

5.4. Regulation of Enzyme Activity

- ● Enzymes can be regulated to control rxn rates through a variety of mechanisms
- ● Why regulation?
  - In multistep metabolic pathways, the slowest step limits the overall rate of the rxn
  - It is therefore most efficient to regulate the metabolic pathway by controlling key enzymes that are involved in this 'rate-limiting' step
- ● Generally, five independent mechanisms are to regulate enzyme activity

1. By **controlling the expression of the enzyme**
   - from the corresponding gene changes; in response to the cell's changing environment or metabolic demands
2. **proteolytic cleavage** of enzymes
   - ☞ Enzymes may be **irreversibly** activated or inactivated by proteolytic enzymes
   - ✓ Hemophilia-A ➘ *caused by a defect in zymogen activation*
3. **covalent modification**
   - ☞ **reversibly** activated or inactivated by covalent modification such as, phosphorylation of a *Ser, Thr, or Tyr* residue

4. **Allosteric regulation** modulates the activity of key enzymes; through reversible binding of small molecules a process that is relatively rapid , hence, the *1st response of cells* to changing conditions
5. The **degradation of enzymes** by:

- ✓ proteases in the lysosome or
- ✓ proteasomes & caspases ➘ highly selective & regulated
- ✓ determines the lifetimes of the enzymes; consequently enzyme activity over a much longer period of time

6. Lipids

6.1. General consideration

- ➢ **Definition**: water insoluble heterogeneous groups of compounds
  - ▪ Most lipids are fatty acids or ester of fatty acid
  - ▪ They are soluble in non-polar solvents such as petroleum ether, benzene, chloroform
- ➢ Biological lipids are a chemically diverse group of compounds
- ➢ **Sparingly solubility** in water
  - are hydrophobic compounds, soluble in organic solvents
- ➢ Most membrane lipids are **amphipathic**; having a non-polar end and a polar end
- ➢ Found either as:
- Compartmentalized (in membrane)
- Droptets(in adepocytes)
- Lipoprotein particles

Biological functions

- Stored forms of energy ←Fats & oils

- Structural elements of biological membranes ← Phospholipids & Sterols
- Other lipids, although present in relatively small quantities, play crucial roles as:

» Enzyme cofactors, -vitamins
» Electron carriers,
» Light absorbing pigments,
» Hydrophobic anchors for proteins, "chaperones"
» to help membrane proteins fold
» Emulsifying agents,
» **Precursors of hormones (steroids and prostaglandins)**
» Hormones (or Precursor of Hrs.)and intracellular messengers
» Dissolve vitamins

6.2. Fatty acids and Glycerol; the monomers of lipids

Fatty acids

☞ Straight chain hydrocarbons possessing a carboxyl (COOH) group at one end
☞ The simplest with structural formula of R-COOH where R = hydrocarbon chain
☞ A 16-C fatty acid: $\underline{CH_3(CH_2)_{14}}$-$\underline{COO^-}$
←Non-polar ← polar
☞ Exists in body free or as fattyacyl esters
☞ Most contain an even number of carbon atoms

Fatty acids fill two major roles in the body:

- as the components of more complex membrane lipids
- as the major components of stored fat in the form of TAG

I. Classification

They differ from each other by

1. Length of the tail
2. Degree of unsaturation
3. Position of double bonds

Classified based on

a. **The no of carbon atom**
   1. Short chain←4-6
   2. Medium chain←8-12
   3. Long chain←>12

b. **Presence or absence of double bond**,
   1. **Saturated**; no double bond
   2. **Unsaturated**; If there is at least one double bond
      - **Monounsaturated fatty acids** contain 1 double bond
      - Found mostly in vegetable oils such as olive, canola & peanut
      - **polyunsaturated fatty acids** (PUFA) have >2 double bonds
      - Found in nuts, vegetable oils such as safflower, sunflower and soybean, and in fatty fish, e.g.
      - linoleic :(18:2,⊗9,12)
      - linoleinic:(18:3, ⊗9,12,15)
      - arachidonic acid :(20:4, ⊗5,8,11,14)

	Carbon Atoms/ Double Bonds	Common Name	mp (°C)
Saturated	12:0	lauric acid	44
	14:0	myristic acid	58
	16:0	palmitic acid	63
	18:0	stearic acid	71
	20:0	arachidic acid	77
Unsaturated	16:1	palmitoleic acid	-0.5
	18:1	oleic acid	16
	18:2	linoleic acid	-5
	18:3	linolenic acid	-11
	20:4	arachidonic acid	-49

C. **Essential Fatty Acids**

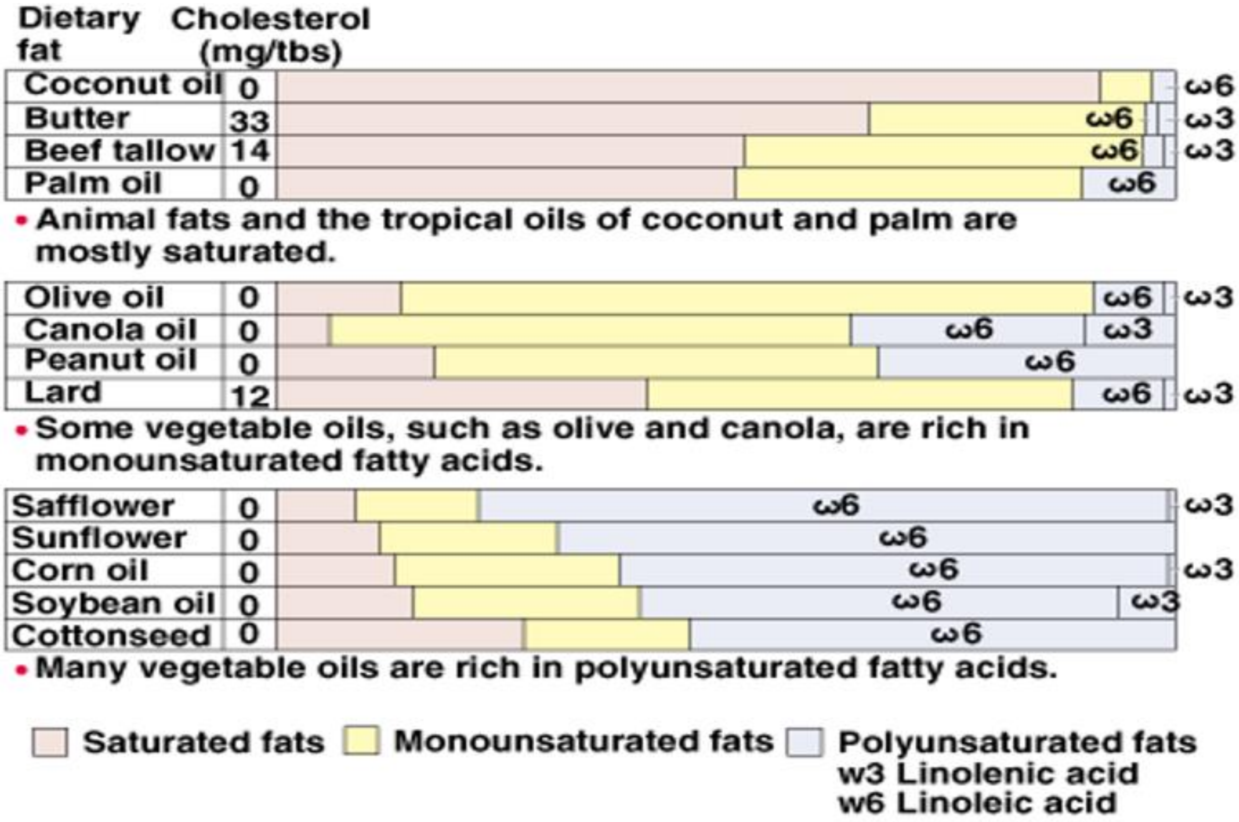
- The body can synthesize all of the fatty acids it needs from carbohydrates, fat or protein except for two:
  1. Linoleic acid(omega 6)
  2. Linolenic acid(omega 3)

The distance of the double bond closest to the ω (omega) end:

- Oleic acid → ω9 FA,
- Linolenic acid → ω3 FA,
- Arachidonic acid → ω6 FA

```
 H   C#    1  2  3   4   5   6   7   8  9  10  11  12  13  14  15  16  17 18
 |
H-C-OH HOO-C-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3 Stearic
 |
H-C-OH HOO-C-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH=CH-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3  Oleic
 |
H-C-OH HOO-C-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH=CH-CH2-CH=CH-CH2-CH2-CH2-CH2-CH3  Linoleic
 |
 H
Glycerol                         3 Fatty Acid Molecules
```

Which fatty acids are more healthy?



III. Physical Properties of FA

- Physical & physiologic properties of FAs reflect: Chain length & degree of unsaturation
- **Physical state**
  - Saturated = solid at RT; often animal source; e.g. lard
  - Unsaturated = liquid at RT; plant source; e.g. vegetable oil
- **Melting point**

  Affected by

  1. the length of the hydrocarbon tails
     - As the length of tails increases, melting points increases due to number of van der Waals interactions.
  2. degree of unsaturation
     - As the degree of unsaturation increases, fatty acids become more fluid--> melting point decreases

6.3. Classification of Lipids

Classified based on:

1. **Function**
   a. Storage -Fats and oils
   b. Structural
   c. and Other
2. **Lipid composition** ← as:
   a) **Simple lipids**; Fats & Oils (TAG) & Waxes

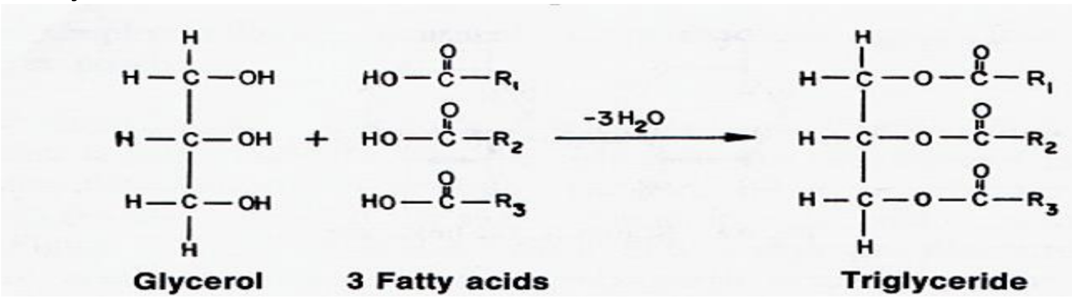
b) **Complex lipids**; Phospholipids, Glycolipids, Lipoproteins & Others, Precursor and derived lipids; Fatty acids, steroids, ketone bodies, lipid-soluble vitamins, etc.

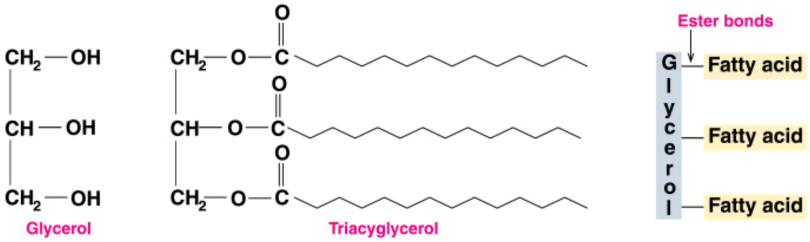
- Oils occur in all parts of a plant, but are most common in seeds. Some seeds have so much oil that it can be commercially harvested. The most commonly used oils are cotton, sesame, safflower, sunflower, olive, coconut, peanut, corn, castor bean, and soybean oils.
- The most common seed oil fatty acids are oleic acid (one double bond), linoleic acid (two double bonds), and linolenic acid (three double bonds). Linoleic and linolenic are essential fatty acids – we can't make them ourselves.

6.3.1. Triacylglycerols(TAG)-lipids in our diets

- the simplest lipids constructed from fatty acids
- also referred to as Triglycerides, Fats, or Neutral fats
- used almost universally as stored forms of energy in living organisms
- Composed of three FAs each in **ester linkage** with a single glycerol;

Glycerol + 3 FFA TG + H_2O





Classified as

1. **Simple** TAGs; those containing the same kind of FA in all three positions
   - E.g., Simple TAGs of 16:0, 18:0, and 18:1,
   - for example, are: Tristearin, Tripalmitin, and Triolein, respectively
2. **mixed** TAGs; they contain 2 or more different Fas
   - Most naturally occurring TAGs are mixed;

6.3.2. Waxes

- ☞ complex mixtures of fatty acids linked to long-chain alcohols.
- ☞ are esters of long-chain (C_{14}-C_{36}) saturated & unsaturated FAs with long-chain (C_{16} to C_{30}) alcohols
- ☞ Melting points (60 to 100 ^oC) are generally higher than those of TAGs
- ☞ Biological waxes find a variety of applications

Source of wax

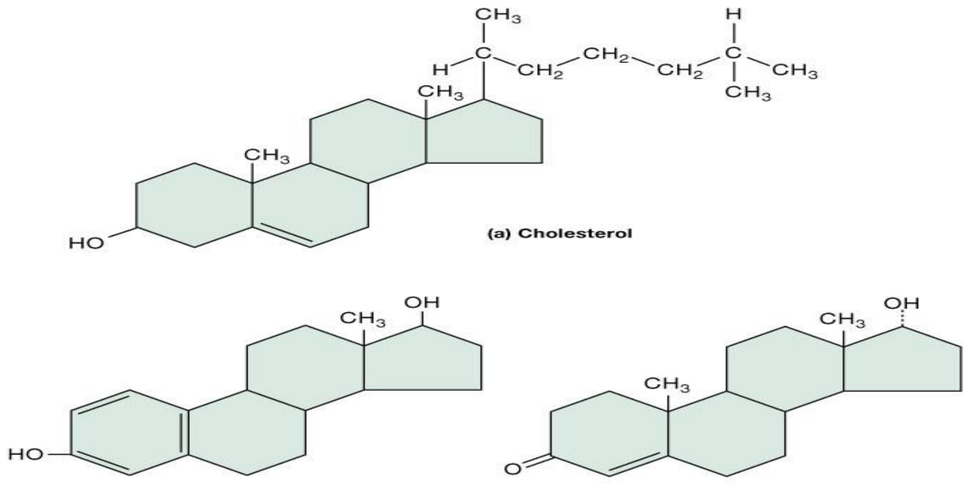
- ☞ Different types of wax exist in plant
  - **Epicuticular** waxes -outermost layer of leaves, fruits, and herbaceous stems
  - **cuticular** waxes -Waxes embedded in the cuticle of the plant
  - **Cutin** - wax in the cuticle and it makes up most of the cuticle.
  - **Suberin** - found in cork cells in bark and in plant roots.
- ☞ Structures of waxes vary depending on which plant produced them.
- Bayberry Wax
- Jojoba Wax

Importance of wax

- ☞ Serve as Energy Stores and Water Repellents
- Waxes are usually harder and more water repellant than other fats
- ☞ Pharmaceutical, cosmetic, and other industries;
- Lanolin (from lamb's wool), beeswax, carnauba wax (from a Brazilian palm tree), and
- ☞ used in the manufacture of **lotions**, **ointments** and **polishes**
  - wax extracted from spermaceti oil (from whales)

Steroids

- Are involved in cell membrane structure
- Include sex hormones and hormones regulating metabolism
- Are important in lipid digestion



(a) Cholesterol

(b) Estrogen

(c) Testosterone

6.5. Structural Lipids in Membranes

- In aqueous solution, phosphoglycerides spontaneously form into a lipid bilayer, with a back-to-back arrangement of lipid monolayers (Figure 6.8)
  - polar head are in contact with the aqueous environment
  - nonpolar tails are buried within the bilayer
  - the major force driving the formation of lipid bilayers is hydrophobic interaction
  - the arrangement of hydrocarbon tails in the interior can be rigid (if rich in saturated fatty acids) or fluid (if rich in unsaturated fatty acids)
- The central architectural feature of biological membranes is:
  - a double layer of lipids
  - w/c acts as a barrier to the passage of
    - polar molecules & ions
- Membrane lipids are amphipathic:
- Hydrophobic & Hydrophilic
- Interactions ←their
- Hydrophobic with each other
- Hydrophilic with water
- Direct their packing into sheets called
- membrane bilayers

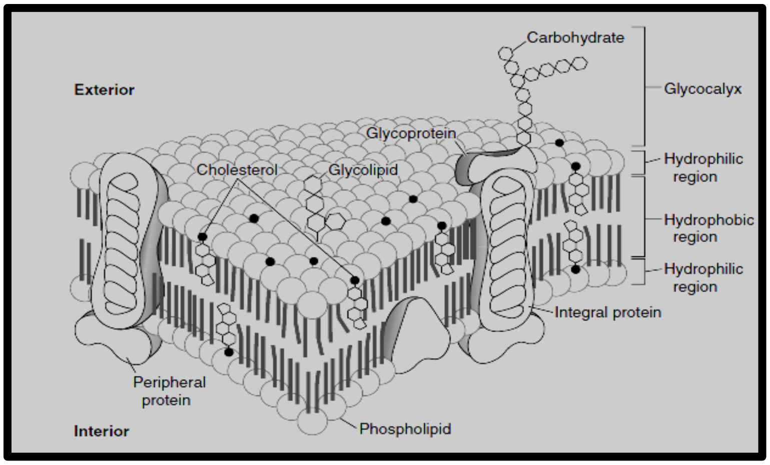


Fig.-pl. Basic structure of an animal cell membrane

Membrane Proteins

- ☞ Functions: transport substances across membranes, receptor sites, and sites of enzyme catalysis
- ☞ Peripheral proteins
  - bound by electrostatic interactions
  - can be removed by raising the ionic strength
- ☞ Integral proteins
  - bound tightly to the interior of the membrane
  - removed by treatment with detergents or ultrasonification
  - removal generally denatures them

Fluid Mosaic Model

- ☞ **Fluid**: there is lateral motion of components in the membrane;

- proteins, for example, “float” in the membrane and can move along its plane

☞ **Mosaic**: components in the membrane exist side-by-side as separate entities
- the basic structure is that of a lipid bilayer with proteins, glycolipids, and steroids such as cholesterol embedded in it
- no complexes, as for example, lipid-protein complexes, are formed

Membrane Transport

Passive transport
- driven by a concentration gradient
- simple diffusion: a molecule or ion moves through an opening created by a channel protein
- facilitated diffusion: molecule or ion is carried across a membrane by a carrier protein

Active transport
- a molecule or ion is moved against a concentration gradient
- see the Na^+/K^+ ion pump (Figs 6.19 - 6.20)

Membrane receptors
- generally oligomeric proteins
- binding of a biologically active substance to a receptor initiates an action within the cell
- see the low-density-lipoprotein (LDL) receptor (Fig. 6.21)
- see the Neuromuscular Junction (Figs 6.22-6.24)

Five general types of membrane lipids:
1. Glycerophospholipids the hydrophobic regions are composed of two FAs joined to glycerol
2. Sphingolipids a single fatty acid is joined to a fatty amine, sphingosine
3. Galactolipids & Sulfolipids also contain two FAs esterified to glycerol, but lack the characteristic phosphate of phospholipids
4. Sterols; Compounds characterized by a rigid system of 4 fused hydrocarbon rings
5. Archaebacterial tetraether lipids; 2 very long alkyl chains are ether-linked to glycerol at both ends

Lipids in horticultural crops
- Lipids comprise less than 1 g/ 100g
- Usually found associated with cuticle
- **Avocado and olive** exceptionally have 20 g and 15 g lipid/100 g as oil droplets in the cells
- The generally low lipid content is seen as a positive factor in combating the rise of heart diseases
- Therefore, increased consumption of fruits and veges is extensively promoted by health authorities
  - **Even high lipid fruits like Avocado and Olive have monounsaturated fats, w/c have been shown not to increase the incidence of heart diseases**

7. Nucleic Acid

LEARNING OBJECTIVES

After reading this chapter you should be able to:

- Compare and contrast
- ✓ purine & pyrimidine
- ✓ nucleoside and nucleotide
- ✓ DNA and RNA
- Describe the composition & structure of DNA & RNA
- The concepts of directionality & complementarity in DNA structure
- Outline the process for packaging of DNA in the nucleus

Cellular nucleic acids

- Exist in two forms Deoxyribonucleic acid (DNA) & Ribonucleic acid (RNA).
- Approximately 90% of the nucleic acid within cells is RNA, the remainder is DNA;
- DNA is the repository of genetic information within the cell.

Function of nucleic acids

- the chemical of life
- contains all the information required to build the cells and tissues of an organism.
- carries along its length a series of coded chemicals called genes

Generelly DNA serves the following functions

- ⇨ It is the genetic material in all prokaryotes and eukaryotes.
- ⇨ It is capable of replication by which it can be faithfully passed on to successive generations.
- ⇨ It is involved in the synthesis of RNA.
- ⇨ It provides the code for protein biosynthesis.
- ⇨ It is involved in mutations and genetic recombinations, which bring about variations.

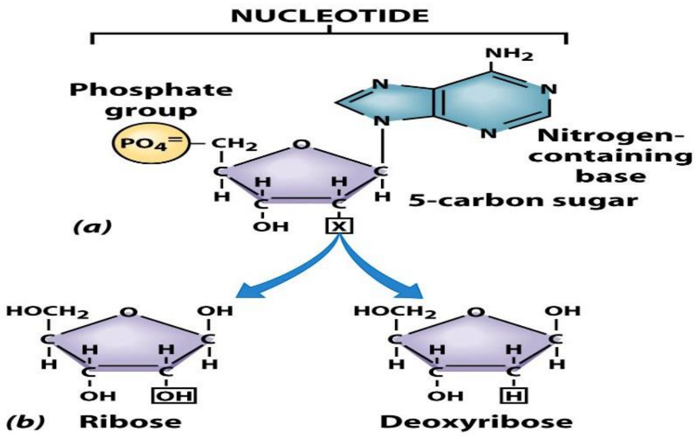
7.1. Components of the nucleic acids

The monomer for all nucleic acids is the nucleotide, which has 3 parts:

- A phosphate group
- A 5-carbon sugar (deoxyribose in DNA or ribose in RNA)
- missing the -OH group at the 2'-position
- A nitrogen-containing base - Adenine (A), Guanine(G), Cytosine (C), Thymine (T); Uracil (U)
- * Thymine is found only in DNA and Uracil only in RNA

Nucleotide Structure

- The monomer units or building blocks of nucleic acids
- Contains three different components
    1. Phosphate group
    2. Nitrogen containing base (A,T,G,C,U)
    3. Five-carbon sugar (ribose or deoxyribose)



N bases (Purines & pyrimidines)

- are nitrogen-containing heterocycles, cyclic compounds
- Has six-atom in the ring

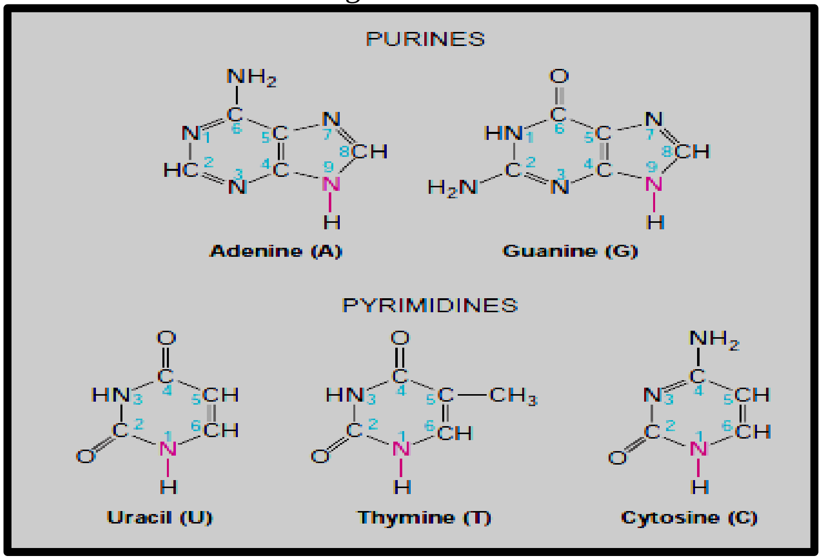
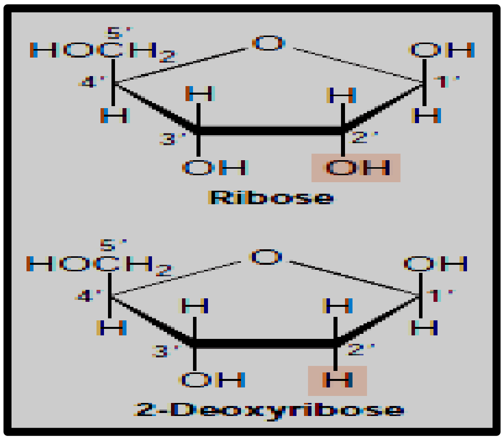


Fig-1b . Chemical Structures of the Principal Bases

Five-carbon sugar (ribose or deoxyribose)



the sugar in ribonucleosides is D-ribose, in deoxyribonucleosides it is 2-deoxy-D-ribose

What is the difference between the two sugar?

- missing the -OH group at the 2'-position of deoxyribonucleosides

Nucleosides

- are derivatives of purines & pyrimidines
- a sugar linked to a ring nitrogen base by **N-glycosidic bond**,

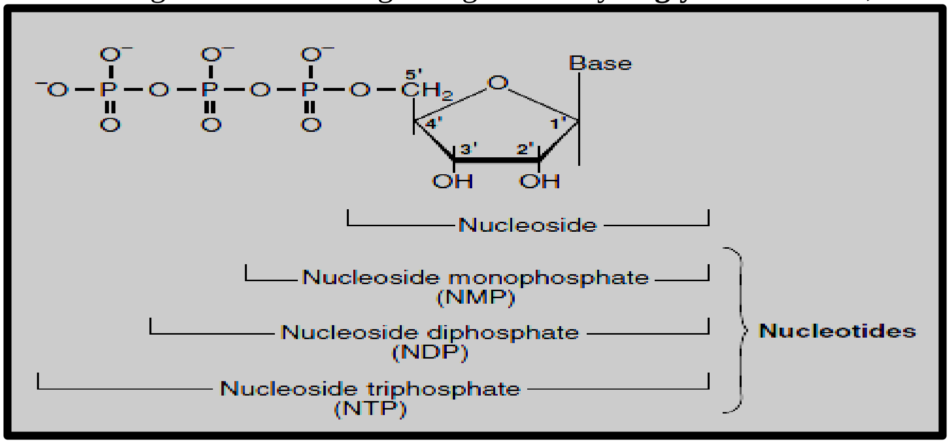


Fig-. Nucleoside & Nucleotide Structures. Shown with Ribose as the Sugar.

The corresponding deoxyribonucleotides are abbreviated dNMP, dNDP, & dNTP. N-any base (A, G, C, U, or T).

		Bases			
		Purines		Pyrimidines	
		Adenine (A)	Guanine (G)	Cytosine (C)	Uracil (U) Thymine [T]
Nucleosides	in RNA	Adenosine	Guanosine	Cytidine	Uridine
	in DNA	Deoxyadenosine	Deoxyguanosine	Deoxycytidine	Deoxythymidine
Nucleotides	in RNA	Adenylate	Guanylate	Cytidylate	Uridylate
	in DNA	Deoxyadenylate	Deoxyguanylate	Deoxycytidylate	Deoxythymidylate
Nucleoside monophosphates		AMP	GMP	CMP	UMP
Nucleoside diphosphates		ADP	GDP	CDP	UDP
Nucleoside triphosphates		ATP	GTP	CTP	UTP
Deoxynucleoside mono-, di-, and triphosphates		dAMP, etc.			

7.2. DNA and RNA structure and their difference

Table-A. The Differences Between DNA & RNA

Characteristic	DNA	RNA
Length	DNA is significantly longer than RNA, b/c it stores all of the genetic information.	RNA is short because it carries one gene at a time.
Number of strands	Two	One
Location in cell	Nucleus only - it is too big to go through the nuclear membrane.	Nucleus & cytoplasm; it can travel everywhere b/c it's more practical than hauling big ol' DNA around whenever we want to make a molecule.
Nitrogenous bases	A, T, C, G	A, U, C, G
Sugar used	Deoxyribose	Ribose
How it's made	DNA replication	Transcription

General Features of RNA

There are 3 major classes of RNA molecules found in cells:

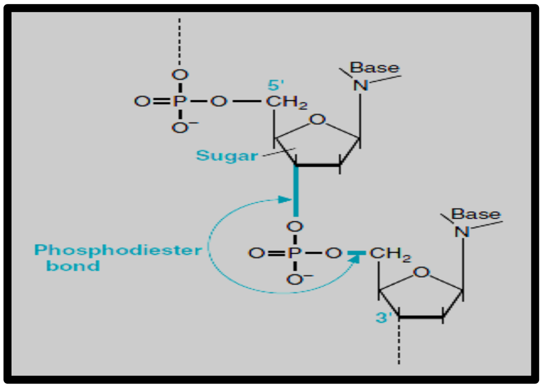
1. ribosomal RNA (rRNA),
2. transfer RNA (tRNA),
3. messenger RNA (mRNA)

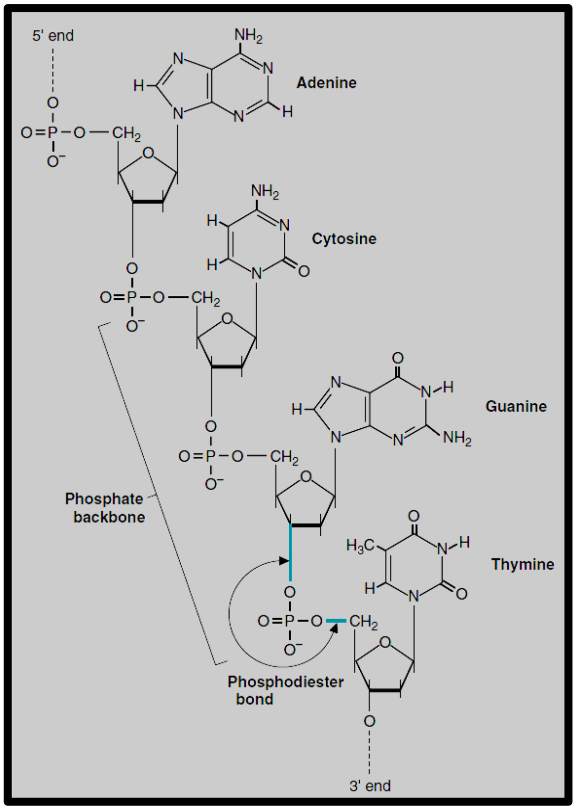
- each class has a distinctive size & function

DNA Structure

☞ The chains of DNA are polymerized through a **phosphodiester** linkage from the 3'-OH of one subunit to the 5'-OH of the next subunit.

- ☞ is a linear deoxyribose phosphate chain with Purine (A & G) & Pyrimidine (C & T) bases attached to C-1 of the deoxyribose





The different structure of DNA

- ☞ single or double stranded
- ☞ circular or opened/linear
- ☞ **Primary structure of DNA**: is the linear sequence of its building nucleotide units
- ☞ **Secondary structure of DNA**: DNA is present in the form of double stranded molecule.

Double stranded linear DNA

- is present in nucleus of body cells
- encodes for the majority of cellular proteins
- it is also present in DNA viruses

Double stranded circular DNA is present in:

- mitochondria & bacterial nuclear
- plasmid DNA

Characteristic of DNA

1. Replicate faithfully and transmit to offspring
2. Stores genetic information, DNA segments called genes
3. Encode directions to make proteins that control cellular growth and metabolism.
4. DNA has the ability to express phenotypically and control cells (by gene expression)
5. DNA is capable of accommodating changes (mutation): DNA contains genetic changes (mutations) that are passed on to offspring.

6. DNA is stable within a living organism

Physical property of DNA

- ☞ Separating the two strand of a DNA double helix
  - Salt effect
  - Temperature effect
  - Chemical denaturant
  - Effect of GC content
- ☞ Rejoining the separated DNA strand
- ☞ Intercalating DNA dyes

8. Plant Metabolism (carbohydrate, lipid and protein)

Learning objectives

- ☞ Define, metabolism, anabolism, catabolism and compare and contrast catabolism and anabolism
- ☞ Glycolysis and pyruvate oxidation
- ☞ Rumen metabolism of carbohydrates and lipids
- ☞ Oxidation of fatty acids and biosynthesis of lipids
- ☞ Oxidation of amino acids and biosynthesis of amino acids and proteins
- ☞ Principles of photosynthesis

8.1. Overview of Metabolism

What is metabolism? what is its importance?

Metabolism is the sum of cellular reactions

- ⇨ The sum total of all the chemical and physical changes/process that occur in a living system
- ⇨ **the entire network of chemical reactions carried out by living cells**
- Transformation of nutrients
- Excretion of waste products
- Energy transformations
- Synthetic and degradative process
- ⇨ Classified into
- **Catabolic** reactions - degrade molecules to create smaller molecules and energy
- **Anabolic** reactions - synthesize molecules for cell maintenance, growth and reproduction
- **Metabolites -** small molecule intermediates in the degradation and synthesis of polymers

Metabolic pathway

- A sequence of consecutives enzymatic reaction that brings about the synthesis, breakdown or transformation of a metabolite from a key intermediate to same terminal compound
- May be linear, cyclic, branched, tiered, directly reversible or indirectly reversible
  1. Leaner metabolic pathway –A-B-C
  2. Cyclic metabolic pathway
     e.g. Citric acid cycle, Nitrogen cycle

Metabolism	Conversion	Occurrence
Glycolysis	Glucose to pyruvate	Cytosol
Krebs' cycle		Mitochondria and cytosol
Gluconeogenesis	Converts Fats & Proteins to Glucose	Germinating Seeds
Calvin cycle	fix CO2 into rubisco & then to trioses, hexoses, & pentoses	Chloroplast
glyoxylate cycle	acetyl-CoA is converted to succinate	Glyoxysomes
®-oxidation	break down fatty acids to acetyl-CoA	

General features of metabolic reactions

- ✍ All metabolic reactions share some general features:
  1. They are catalyzed by enzymes
  2. They are universal in that all organisms show remarkable similarity in the main pathways.
  3. They involve relatively few types of chemical reaction.
  4. They are controlled, often by modulation of key regulatory enzymes.
  5. The pathways that break particular molecules down are different from those used to synthesize them.

Metabolism in plant and animals

Compare and contrast metabolism in plant and animals? What are the unique nature of plant metabolism?

In eukaryotes different sets of metabolic reactions are carried out in different organelles. In animals and plants this compartmentalization is carried further, so that in some cases different reactions take place in different body organs. Prokaryotes too show compartmentalization of a simpler sort—some processes are associated with regions on the inner face of the cell membrane..

Carbohydrate Metabolism in a Typical Plant Cell

- ☞ More complex in several ways than that in a typical animal cell

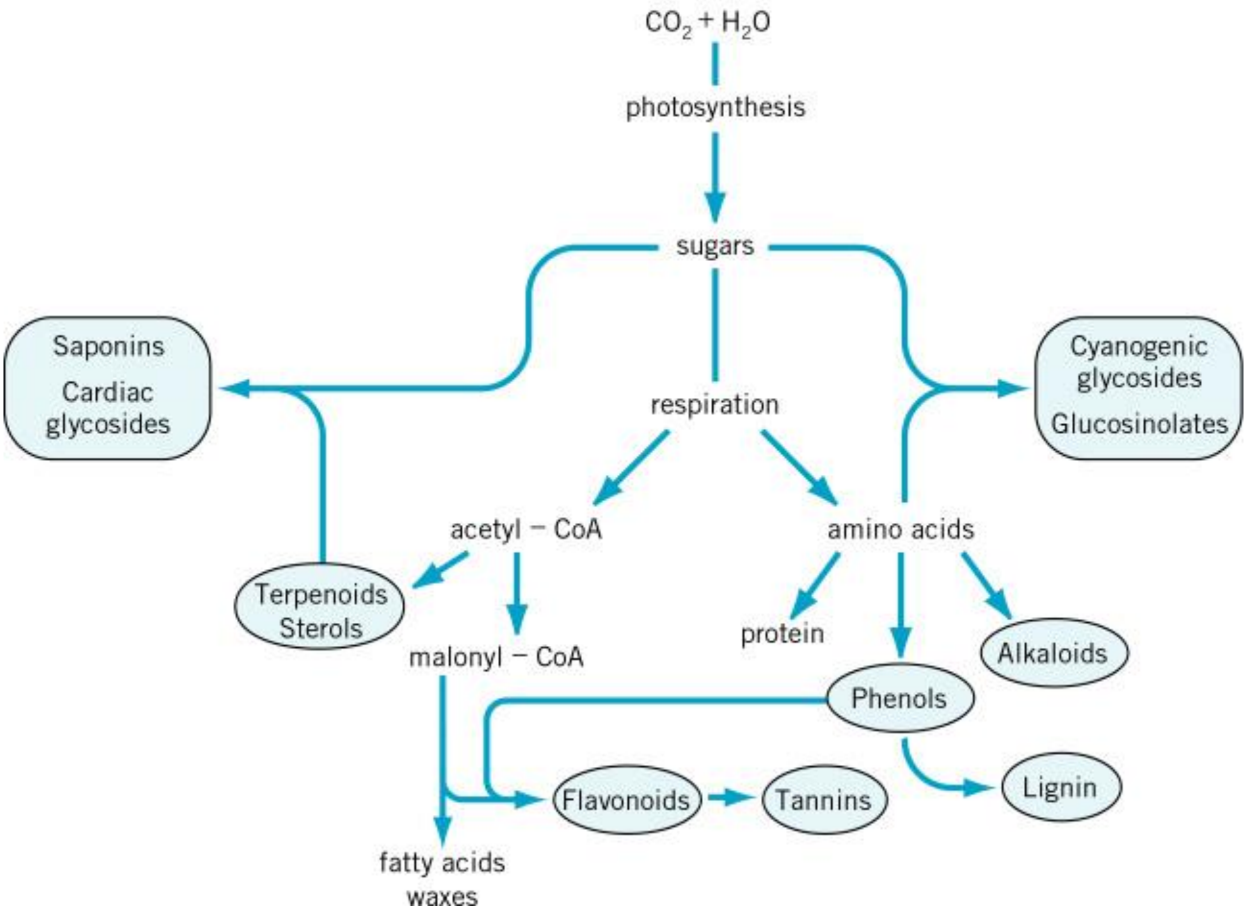
Common metabolism pathway:

- – glycolysis,
- – Krebs' cycle,
- – oxidative phosphorylation;
- – Gluconeogenesis

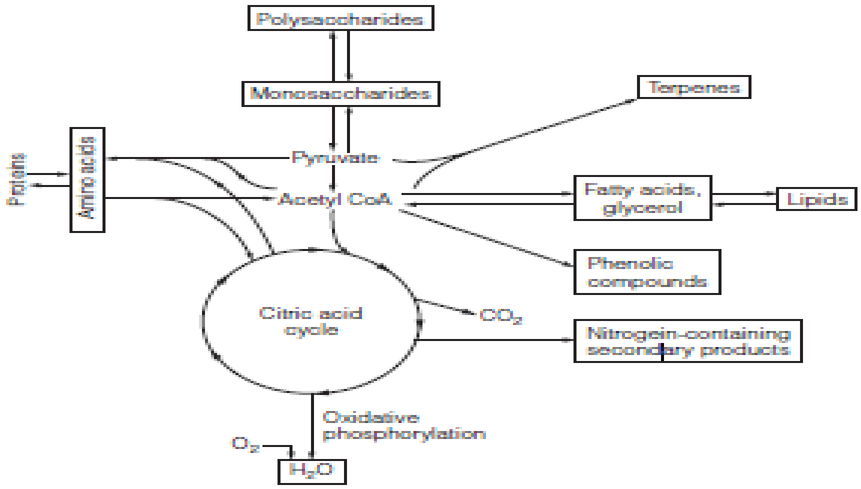
Only in plant

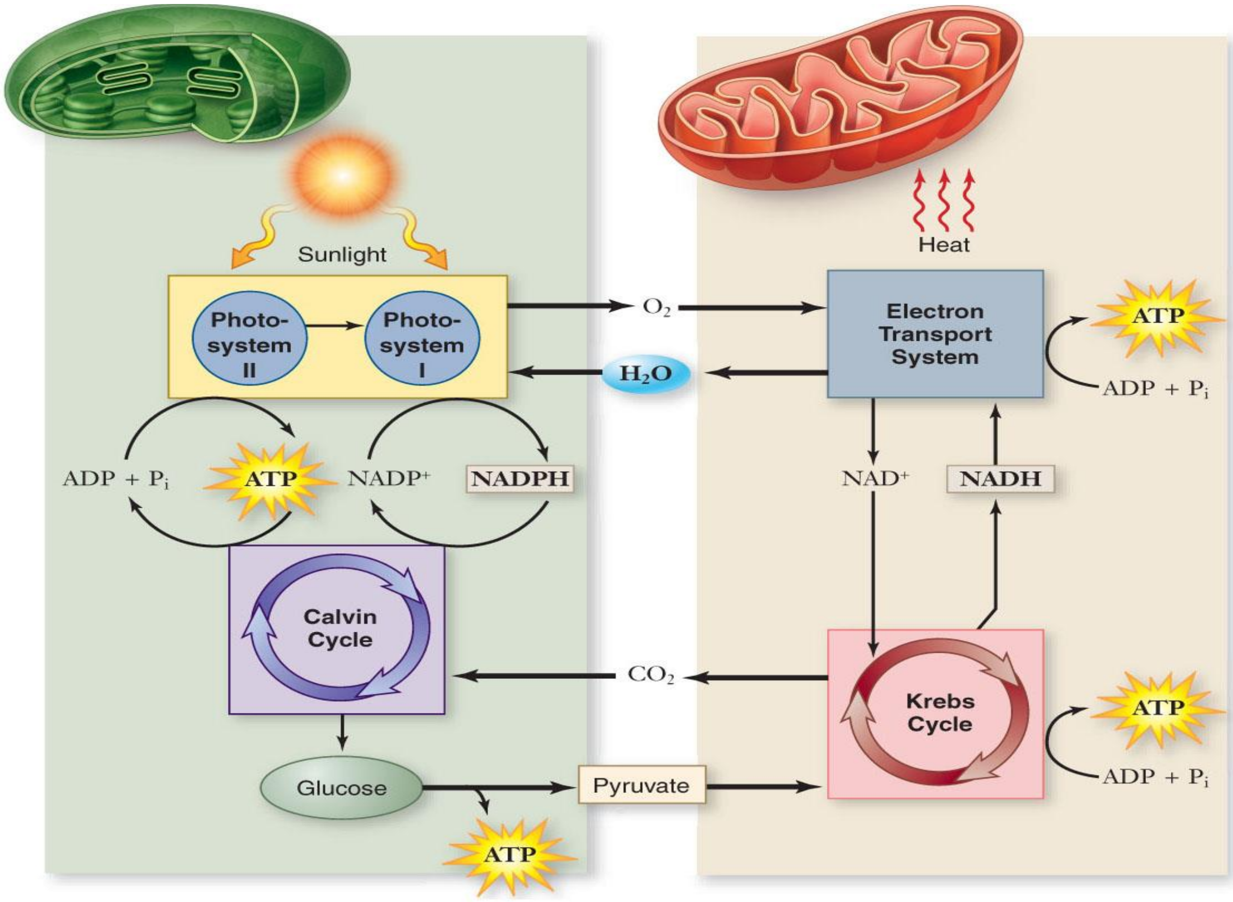
- Calvin cycle
- glyoxylate cycle
- starch synthesis in amyloplasts
- organic acid storage in vacuoles

Overview of plant metabolism



The overview of plant metabolism





8.2. Carbohydrate Metabolism

- Glycogenesis - conversion of glucose to glycogen; stimulated by insulin
- Glycogenolysis - hydrolysis of glycogen to form glucose; stimulated by glucagon
- Gluconeogenesis - synthesis of glucose from non-carbohydrates such as fats and amino acids

1. Glycolysis

- Definition: From the Greek: glykys→"sweet" & lysis → "splitting".
- It is a near-universal pathway: by which a Glc molecule is degraded in a series of enzyme-catalyzed rxn's to yield two molecules of pyruvate
- A series of 10 enzyme-catalyzed reactions by which glucose is oxidized to two molecules of pyruvate.

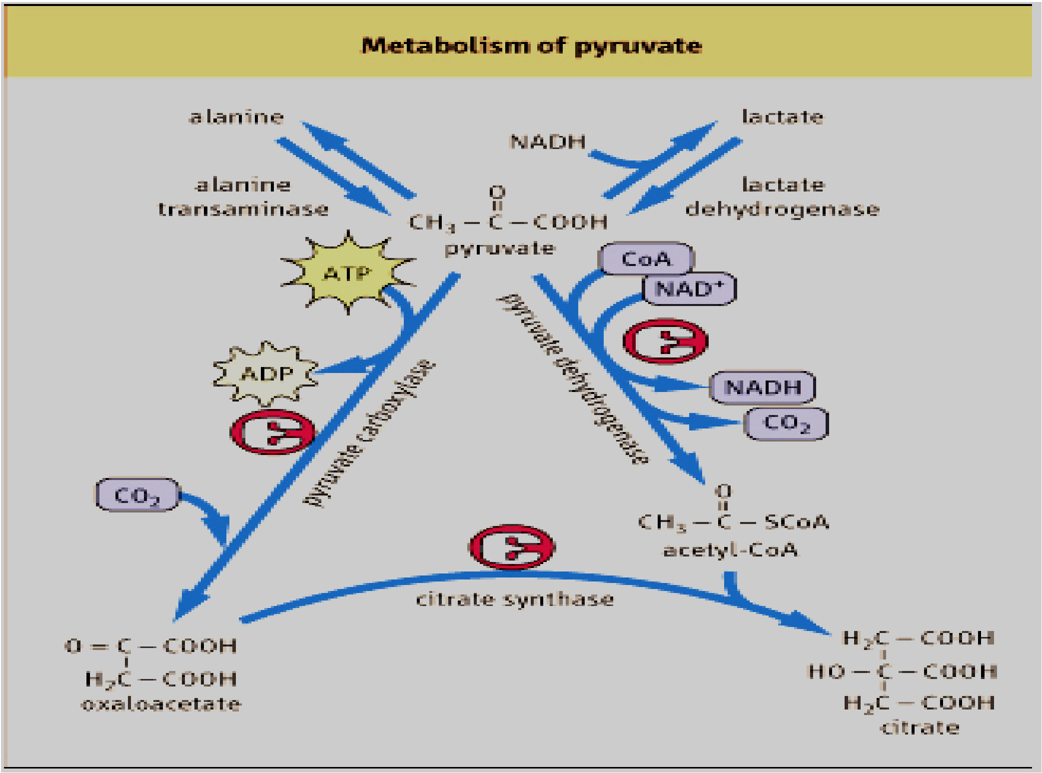
$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{glycolysis}} \underset{\text{Pyruvate}}{2CH_3\overset{O}{\overset{\|}{C}}COO^-} + 2H^+$$

During glycolysis, there is net conversion of 2ADP to 2ATP.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + 2ADP + 2P_i \longrightarrow \underset{\text{Pyruvate}}{2CH_3\overset{O}{\overset{\|}{C}}COO^-} + 2ATP$$

Pyruvate:

- is at a crossroads in metabolism
- It may be converted into:
  - Acetyl CoA (PDHC)
  - Lactate (LDH)
  - Alanine (ALT)
  - Oxaloacetate (PC)
- Depending on metabolic circumstances pyruvate may be Routed toward:
  - TCA cycle
  - Gluconeogenesis
  - Fatty acid biosynthesis



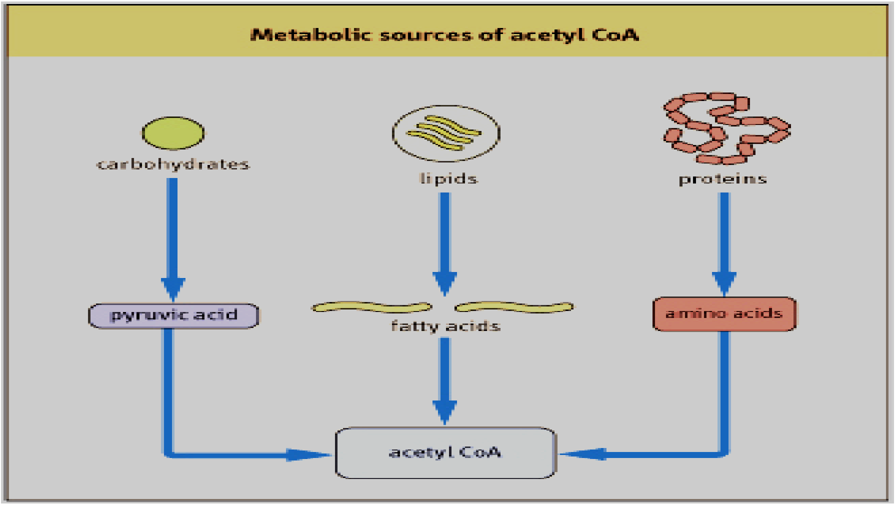
2. Krebs Cycle (Citric Acid Cycle)

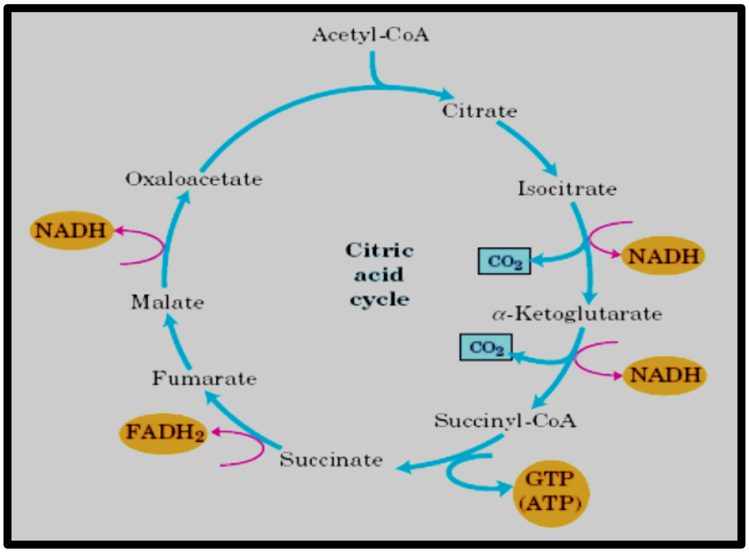
- In the presence of oxygen, pyruvic acid produced in glycolysis passes to the second stage of cellular respiration, the **Krebs cycle**.
- Frequently called
- The **Krebs' cycle**; b/c Sir Hans Krebs first formulated its rxn's into a cycle
- It is also called the **"citric acid cycle"** b/c citrate was one of the first compounds known to participate
- The most common name for this pathway **Tricarboxylic acid (TCA) cycle**:
    - denotes the involvement of the tricarboxylates citrate & isocitrate

What happens during the Krebs cycle?

Formation of Acetyl-CoA:

- a common product of many catabolic pathways
- TCA cycle begins with acetyl-CoA; w/c has three major metabolic precursors:
    - Carbohydrates
    - Lipids
    - Amino acids





Biological importance of Krebs' cycle

- Energy production -Used for the generation of ATP
- Acetyl CoA, pyruvate and citric acid cycle intermediates
- are the starting point for the production of amino acids, lipids, polysaccharides and secondary products
- It provides intermediates for synthesis of non-essential amino acids
  - Uses oxidative phosphorylation to turn NADH into ATP
  - requires oxygen and electrons; thus the rate of ATP generation is limited by oxygen or electrons
- is a common pathway for metabolism of all fuels in the mitochondrion
- It oxidative strips electrons from fat, carbohydrate & protein fuels;
- Producing the majority of the reduced coenzymes;

Electron Transport Chain

- ☞ The higher negative charge in the matrix attracts the protons (H^+) back from the intermembrane space to the matrix.
- ☞ The accumulation of protons in the intermembrane space drives protons into the matrix via diffusion.
- ☞ Most protons move back to the matrix through ATP synthase.
- ☞ ATP synthase is a membrane-bound enzyme that uses the energy of the proton gradient to synthesize ATP from ADP + P_i.
- ☞ The electron transport chain uses the high-energy electrons from the Krebs cycle to convert ADP into ATP.

The Glyoxylate Pathway

- ☞ Conversion of fat to carbohydrates
- ☞ a variation of the tricarboxylic acid cycle,
- ☞ centers on the conversion of acetyl-CoA to succinate for the synthesis of carbohydrates.
- ☞ occurring in plants, bacteria, protists, and fungi.
  - In microorganisms, the glyoxylate cycle allows cells to utilize simple carbon compounds as a carbon source when complex sources such as glucose are not available.
  - The cycle is generally assumed to be absent in animals, with the exception of nematodes at the early stages of embryogenesis.
- ☞ Enables Plants and Bacteria to Grow on Acetate
  - able to subsist on acetate or other compounds that yield acetyl CoA.
  - converts two-carbon acetyl units into four-carbon units (succinate) for energy production and biosyntheses.

What is the different between citric acid cycle and glyoxylate cycle

  - ***glyoxylate cycle*** bypasses the two decarboxylation steps of the citric acid cycle.
  - Another key difference is that two molecules of acetyl CoA enter per turn of the glyoxylate cycle, compared with one in the citric acid cycle.
- ☞

glyoxylate cycle

Isocitrate (C_6) is split into succinate (C_4) and glyoxylate (C_2), preserving the two carbon atoms.

Glyoxylate (C_2)then reacts with acetyl CoA (C_2) to form malate (C_4) and subsequently oxaloacetate which can move on to glucose, leaving succinate to provide the carbon skeleton for continuation of the TCA cycle.

Before photosynthetic mechanisms have developed how plant cell get energy for their metabolic activities?

Gluconeogenesis

- Converts Fats & Proteins to Glucose in Germinating Seeds
- Many plants store lipids & proteins in their seeds

    - sources of energy
    - biosynthetic precursors during germination,
- Active gluconeogenesis in germinating seeds provides:
    - glucose for the synthesis of sucrose, polysaccharides, & many metabolites derived from hexoses

- In plant seedlings, sucrose provides much of the chemical energy needed for initial growth

What is the different between gluconeogenesis in plant and animal?

- Animal cells can carry out gluconeogenesis
    - from three- & four-carbon precursors,
    - but not from the two acetyl carbons of acetyl-CoA
- Because the pyruvate dehydrogenase rxn is effectively irreversible,
    - animal cells have no way to convert:
        - acetyl-CoA to pyruvate or oxaloacetate

Glucogenic amino acids derived from:

- the breakdown of stored seed proteins
- also yield precursors for gluconeogenesis

8.3. Oxidation of amino acids and biosynthesis of amino acids and proteins

Amino acid biosynthesis

- Plants make amino acids from the products of photosynthesis through a very complex process involving the acquisition of N, usually in the form of NH_4, and involving the use of large amounts of energy, in the form of ATP and NADPH.
- Production of **amino acids** and other nitrogen-containing compounds is directly linked to the assimilation of nitrogen by the plant.
- **Nitrogen** is taken up as either nitrate or ammonium, linked to the assimilation of nitrogen by the plant.
- Nitrate is converted to ammonium by nitrate reductase
- ammonium is then incorporated into glutamine and glutamate, either by
- the glutamine synthase-glutamate synthase (GS-GOGAT) pathway or by glutamate dehydrogenase (GDH). Ammonium is toxic and is converted to organic nitrogen compounds in the root. Nitrate may be converted to
- ammonium in the roots, or is carried to shoots and leaves and either
- stored in the vacuole or converted to ammonium. Other amino
- compounds are formed by transamination reactions.

Nitrate assimilation

- Nitrate to nitrite to ammonia
- Essential for the synthesis of organic matter
- Occur in leaf and roots
- Take place in cytosol

- The end product is the whole spectrum amino acids
- Ammonia to amide to aspartate
- Stored as protein (globuline, prolamins, 2s-protein)

Sulfate assimilation

- Enable the synthesis of sulfure containing substance (glutathione, methionine)
- Proceeds primarily by photosynthesis
- Has some parallels to nitrogen assimilation
- Sulfate is active prior to reduction
- Sulfite reductase is similar to nitrate reductase
- H2s is fixed in the form of cysteine to prethionine

Synthesis and breakdown of proteins

Digestion and Absorption of Protein

- ☞ Stomach acid and enzymes facilitate the digestion of protein.
- ☞ It is first denatured, then broken down to polypeptides.
- ☞ The small intestine continues to break down protein into smaller peptides and amino acids so it can be absorbed.
- ☞ Protein Digestion
  - In the Stomach
    - Protein is denatured by hydrochloric acid.
    - Pepsinogen (a proenzyme) is converted into its active form pepsin in the presence of hydrochloric acid.
    - Pepsin cleaves proteins into smaller polypeptides.
    - In the Small Intestine
    - Proteases hydrolyze protein into short peptide chains called oligopeptides, which contain four to nine amino acids.
    - Peptidases split proteins into amino acids.
- ☞ Protein Absorption
  - Used by intestinal cells for energy or synthesis of necessary compounds
  - Transported to the liver
  - Taking enzyme supplements or consuming predigested proteins is unnecessary

Protein synthesis and breakdown in plant

- ☞ Proteins make up most of the remaining biomass of living plant cells.
- ☞ A protein consists of one or more polypeptides made up of amino acids.
- ☞ Plants make amino acids from the products of photosynthesis through a very complex process involving the acquisition of N, usually in the form of NH_4, and involving the use of large amounts of energy, in the form of ATP and NADPH.
- ☞ Proteins are converted into substances than can enter the Kreb's cycle by
    - deamination - loss of (NH_2) from amino group
    - decarboxylation - loss of CO_2 molecule

- dehydrogenation - loss of hydrogen atom

☞ Protein synthesis involves transcription and translation

☞

1. **Fumarate pathway**
- A carbonic pathway where either phenyl-alanine or tyrosine are converted to fumaric acid which then feeds into citric cycle
2. **Oxaloacetate pathway**
- Aspartic and asparagine convert into oxaloacetic acid which then feeds into citric cycle
3. **Succinate pathway**
- Methionine isoleucine and valine are converted to succinic acid which then feeds into citric cycle
4. **α -keto glutarate pathway**
- Arginine, prorine, histidine, glutamine and glutamic acid enter the cirtic acid cycle by way of α -keto glutaratic acid

8.4. Oxidation of fatty acids and biosynthesis of lipids

Lipid biosynthesis- Lipolysis

☞ Hydrolysis of triglycerides into glycerol and fatty acids
☞ Glycerol converted to G 3-P and then into pyruvic acid, then into the Kreb's cycle
☞ Beta -oxidation of fatty acids occurs forming two-carbon fragments which is then attached to coenzyme A, forming acetyl CoA
☞ Plants synthesize a wide variety of lipids, including
- membrane lipids, cuticular waxes
- seed storage lipids (mostly triacylglycerols).

☞ Synthesis of glycerolipids occurs in two stages:
1. addition of the fatty acid chains to glycerol-3-phosphate
2. addition of a head group.

☞ Triacylglycerols
- consist of a glycerol to which three fatty acid chains have been added and
- are synthesized in the endoplasmic reticulum.

☞ They are stored in oil bodies,
☞ small lipid droplets with a surrounding coating of lipid and protein

Plants use acetyl CoA as the basic building block for assembling **long-chain fatty acids**.

Sucrose, polysaccharides and starch

Plant cells produce monosaccharides, from 3-carbon trioses to 6-carbon hexoses. Sucrose is a disaccharide, made of glucose and fructose. Starch is a polysaccharide made up of -(1–4) and -(1–6) branched D-glucose residues. Cellulose is made up of -D-glucose. Sucrose is synthesized in the cytoplasm either by sucrose phosphate synthase and sucrose phosphate phosphatase or by sucrose synthase.

Plant secondary products

ATP synthesis

The Regeneration of ATP

- ATP is a renewable resource that is regenerated by addition of a phosphate group to adenosine diphosphate (ADP)

- The energy to phosphorylate ADP comes from catabolic reactions in the cell
- The ATP cycle is a revolving door through which energy passes during its transfer from catabolic to anabolic pathways

In the electron transport system

NADH = 3 ATP

$FADH_2$ = 2 ATP

1. **ATP Energy from Glycolysis**

   Glucose 2 pyruvate + 2 ATP + 2 NADH

   NADH in cytoplasm $FADH_2$ mitochondria

   Glucose 2 pyruvate + 6 ATP

2. **ATP Energy from Pyruvate**

   2 pyruvate 2 acetyl CoA + 2 CO_2 + 2 NADH

   2 pyruvate 2 acetyl CoA + 2 CO_2 + 6 ATP

3. **ATP Energy from Citric Acid Cycle**

One turn of the citric acid cycle

3 NADH	x 3 ATP	=	9 ATP
1 $FADH_2$	x 2 ATP	=	2 ATP
1 GTP	x 1 ATP	=	1 ATP
	Total	=	12 ATP

Glucose provides two acetyl COA molecules for two turns of citric acid cycle

2 acetyl CoA 24 ATP + 4 CO_2

ATP from Glucose

For 1 glucose molecule undergoing complete oxidation

Glycolysis	6 ATP
2 Pyruvate to 2 Acetyl CoA	6 ATP
2 Acetyl CoA to 4 CO_2	24 ATP

Glucose + 6 O_2 6 CO_2 + 6 H_2O + 36 ATP

ATP accounting

- Glycolysis 2 ATP
- Kreb's cycle 2 ATP
- Electron Transport Chain yields ~34 ATP from 1 glucose!

- Life takes a lot of energy to run, need to extract more energy than 4 ATP!

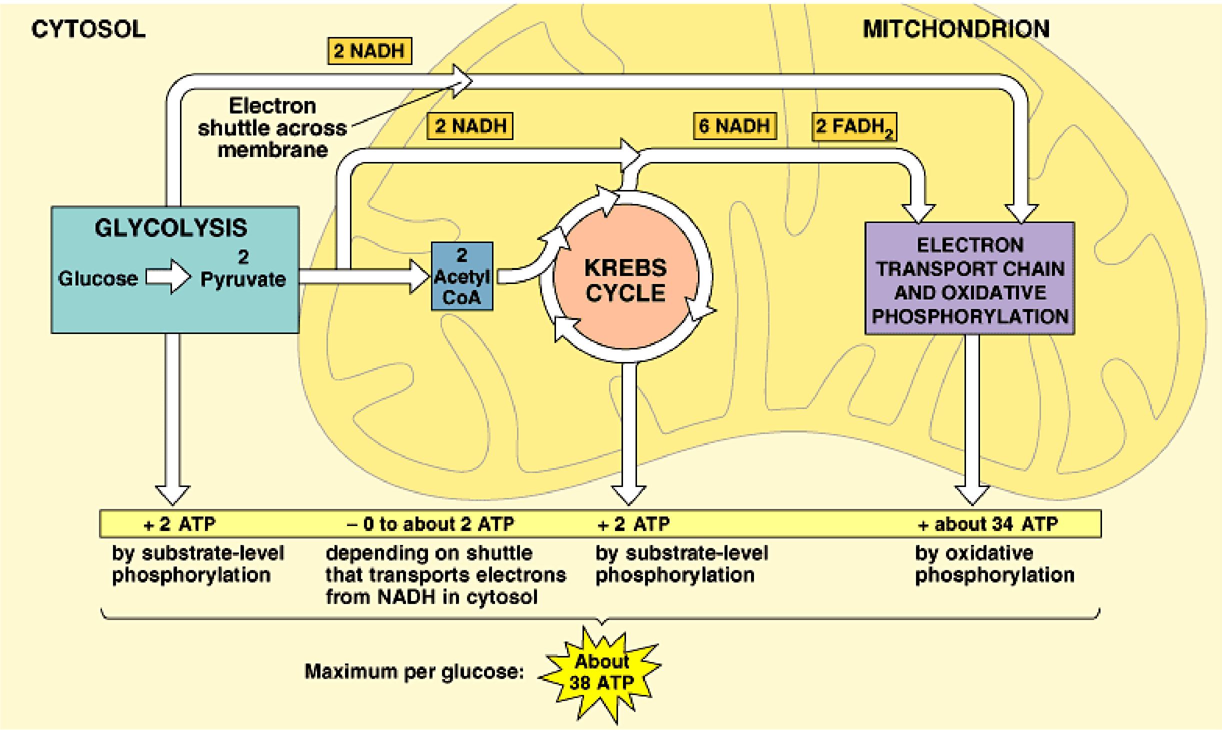


Table 1. The maximum overall energy yield from the oxidation of one molecule of glucose

	Cytosol	Matrix of mitochondrion	Electron transport and ATP synthesis	Total
Glycolysis	2ATP 2NADH		 4ATP	2ATP 4ATP
Pyruvate to acetyl CoA		2NADH	6ATP	6ATP
Citric acid cycle		2ATP 6NADH 2FADH2	 18ATP 4ATP	2ATP 18ATP 4ATP
				36ATP

Comparing Photosynthesis and Cellular Respiration

1. The energy flows in photosynthesis and cellular respiration take place in opposite directions

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

Energy

$$6O_2 + C_6H_{12}O_6 \longrightarrow 6CO_2 + 6H_2O$$

Energy

2. On a global level, photosynthesis and cellular respiration are also opposites.

- Photosynthesis removes carbon dioxide from the atmosphere and cellular respiration puts it back.
- Photosynthesis releases oxygen into the atmosphere and cellular respiration uses that oxygen to release energy from food

8.5. Overview of Photosynthesis

❖ **Energy for all life on earth ultimately comes from photosynthesis**

- Capturing sunlight to provide energy for life on earth
- Autotrophic Process: Plants and plant-like organisms make their energy (glucose) from sunlight.
- Stored as carbohydrate in their bodies.
- $6CO_2 + 6H_2O$ + sunlight ❼ $C_6H_{12}O_6 + 6O_2$

Requirement for photosynthesis

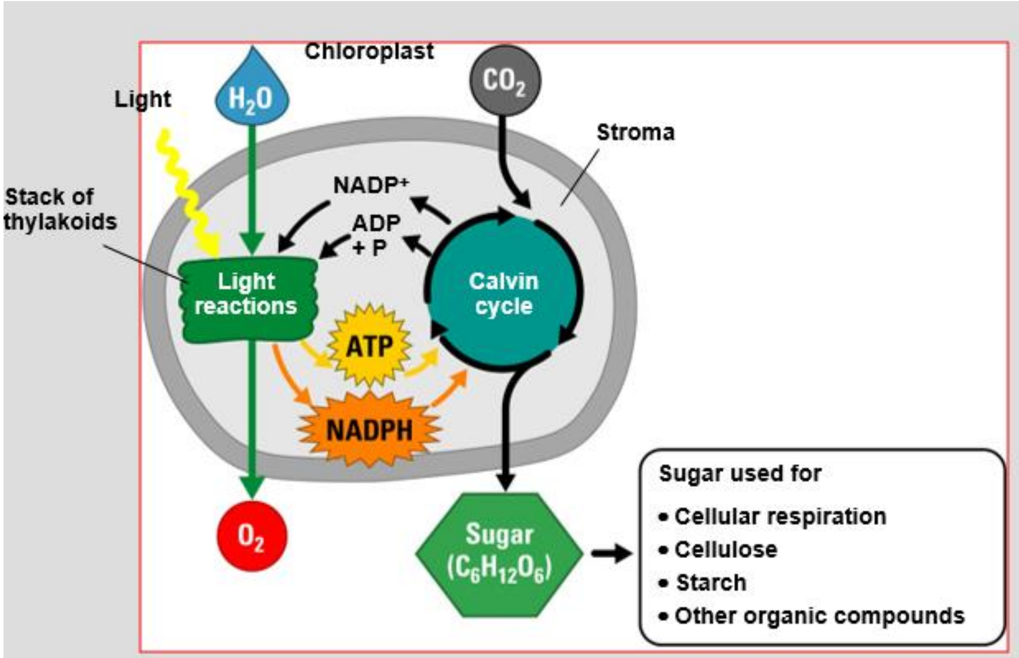
How do plants get the necessary ingredients of photosythesis?

- CO2 is obtained through adjustable pores called **stomata**
- Water and minerals provided by a system of veins
- Veins also carry sugars to other parts of the plant
- Sunlight as an Energy Source- **photon**
- Light is the energy source to drive the synthesis of carbohydrate.
  - Light consists of tiny packets of energy called **photon**
- **Light absorbing pigment(Chlorophyll)**
  - absorbs specific wavelengths of visible light(fig)
  - in photosystems absorb light energy and release electrons

Steps of Photosynthesis

1. light reactions (require light energy
   - capture energy from sunlight
   - convert solar energy to chemical energy
   - Produce ATP & NADPH
2. dark reactions (require chemical energy)
   - ☞ use ATP and NADPH to synthesize organic molecules from CO2
     - ATP generated by the light reactions provides the energy for sugar synthesis
     - The NADPH produced by the light reactions provides the electrons for the reduction of carbon dioxide to glucose
   - ☞ Occur during day time but not directly depend on light
   - ☞ makes sugar from carbon dioxide

Photosynthesis uses light energy to make food molecules



A summary of the chemical processes of photosynthesis

Photosynthetic pathways

There are 3 major pathways by which atmospheric CO2 can be assimilated in photosynthesis

1. C3 photosynthesis(Calvin Cycle) 3-phosphosythetic acid(PGA)
2. C4 photosynthesis(OAA, oxaloacetate)
3. CAM photosynthesis-Crassulacean Acid Metabolism

C4 vs C3 plants

- Km for Rubisco is higher in C4 plants

-> lower affinity for CO2, carboxylation reaction proceeds faster with same amount of enzyme

- C3 plants have lower Km, higher affinity for CO2 -> carboxylation proceeds more slowly

- The C4 pathway is energetically more expensive than C3
  • Under high light, the C4 pathway is favored

Phosphorylation

The introduction of a phosphate group into a compound through the formation of an ester bond between the compound and phosphoric acid

8.6. Metabolite

- Any reactant, intermediate, or product in the reaction of metabolism.
- Classified as

1. **Primary metabolites**
   - Involved in those processes that are necessary for maintenance and survival
   - Includes metabolites involved in the processes of
   - Growth(biosynthesis)
   - Energy production and transformation

- Turnover of cellular components
  - Includes Sugars, amino acids and nucleotides

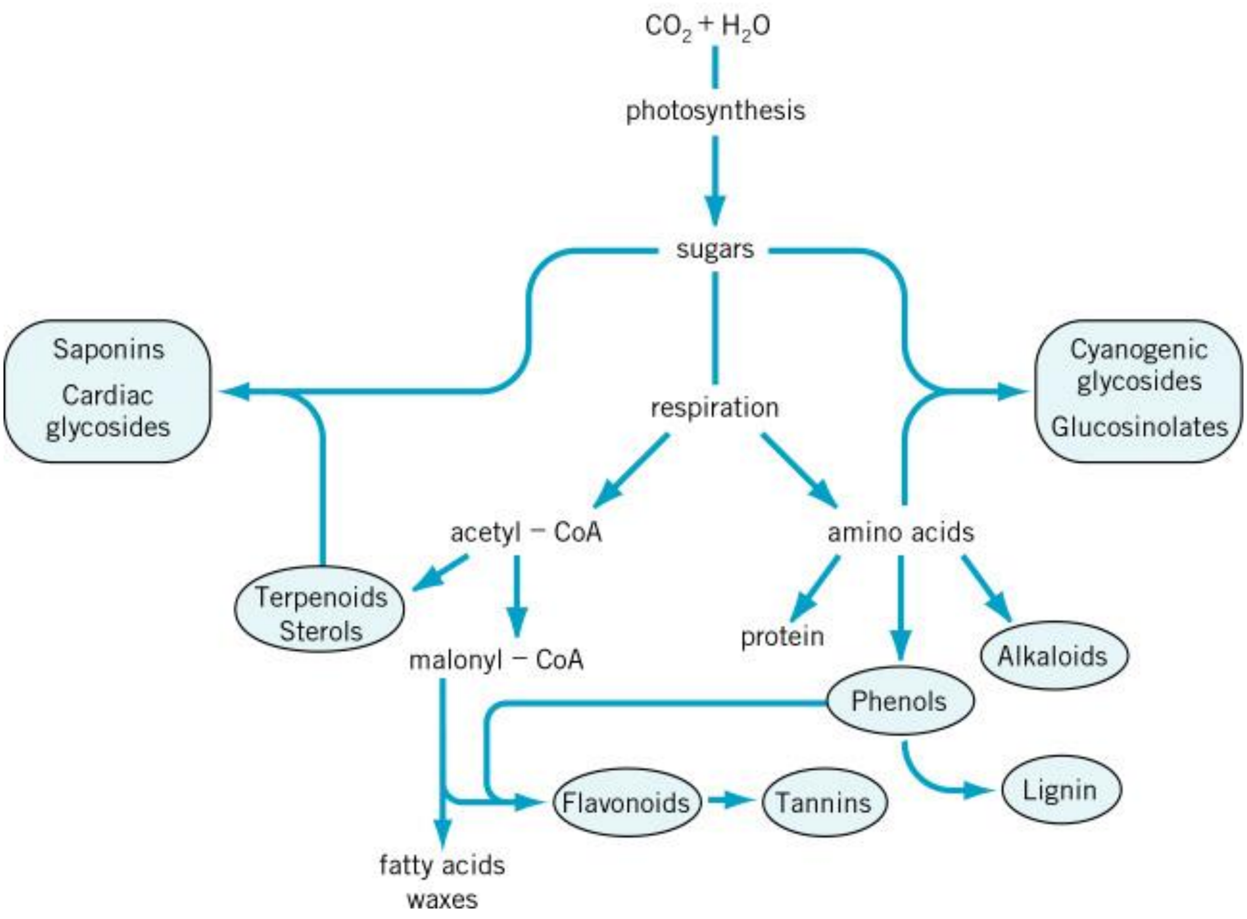
2. **Secondary metabolites**

- Occur only in certain organisms and serve no apparent biological function in the life of the organisms that produce them
- Such as pigments, alkoids, antiiotics, terpenes, and so on
- In plant
- includes Alkaloids,Terpenoids,phenols,glucosinolates etc.

Importance

- Protect plants from the attacks by predators, pathogens, or competitors
- Attract pollinators or seed dispersal agents
- Important for abiotic stresses
- Medicine
- Industrial additives(food,

Secondary metabolites are derived from primary metabolites



9. Phytohormones

Objectives

Be able to state the name of the plant hormone(s) that is (are):

1. Know the five major classes growth regulators.
2. Be able to describe the general functions of each class of growth regulators
3. Describe why they control growth and their character

9.1. General information about Enzymes

Although photosynthesis supplies the carbon and respiration supplies the energy for plant growth, a group of chemicals produced by plants known as plant growth regulators or plant hormones control the growth and development of plants. These chemicals act on plant processes at very low concentrations. Often they are produced at one location and transported to another where they exert their influence (a signaling molecule released by one cell and transported to TARGET CELLS (usually nonadjacent). The target cell contains receptor sites); however, they may also act on the same tissue in which they are produced.

- Also called Plant hormones, Plant Growth regulators (PGRs), growth factors or growth hormones plant growth substances'
- ✓ The word hormone is derived from Greek, meaning *set in motion*.
- are chemicals signal that regulate plant growth and development
- ✓ regulate cellular processes
- ✓ determine the formation of flowers, stems, leaves, the shedding of leaves, and the development and ripening of fruit.
- ✓ shape the plant, affecting seed growth, time of flowering, the sex of flowers, senescence of leaves, and fruits.
- ✓ They affect which tissues grow upward and which grow downward, leaf formation and stem growth, fruit development and ripening, plant longevity, and even plant death.
- ⇨ vital to plant growth, and, lacking them, plants would be mostly a mass of undifferentiated cells

Where and when plant produce hormone?

Plants, unlike animals, lack glands that produce and secrete hormones. Instead, each cell is capable of producing hormones. They are naturally produced within plants, though very similar chemicals are produced by fungi and bacteria that can also affect plant growth.]A large number of related chemical compounds are synthesized by humans.

How they regulate growth and development?

- ⇨ Triggers/control enzyme activities
- ⇨ affect gene expression and transcription levels,
- ⇨ affect cellular division and differentiation,
- ⇨ affect growth and development

Characteristics

- – act on plant processes at very low concentrations
- – produce at one location and act in other location

  Often they are produced at one location and transported to another where they exert their influence (a signaling molecule released by one cell and transported to TARGET CELLS (usually nonadjacent). The target cell contains receptor sites); however, they may also act on the same tissue in which they are produced.

6.2. Basic types of hormone

1. Gibberellins

- ☞ promote growth
- ☞ regulate height
- - Too little- dwarf
- - Too much- long, spindly
- ☞ moves upward and downward in vascular system

- ☞ important in ***bolting*** (sudden stem lengthening)
- ☞ induce seeds of some grasses to germinate (breaks dormancy)
- can break dormancy in buds
- ☞ can stimulate flowering in mature plant

2.Auxins

- ➢ Moves only downward but gravity does not cause its movement.
- ➢ It is generally produced by apical shoot meristems and developing leaves.
- ➢ Promotes growth by stimulating cell elongation.
- ➢ It triggers enzyme activities that loosen the cell wall fibers (normally tightly woven)
- ➢ Stimulates cell division.
- ✓ It activates the vascular cambium and promotes the formation of lateral roots by the pericycle.
- ➢ Inhibits the growth of lateral buds.
- ➢ Inhibits roots
- ✓ Small quantities promote root growth. Slight increases inhibit it.

Auxin production by seeds stimulates fruit growth. If eggs are not fertilized, ovules do not become seeds and auxin cannot be produced. The lack of auxin results in abscission of the flower.

Auxin also prevents fruits and leaves from off prematurely. It can be sprayed on to prevent from falling off.

high concentration uncontrolled growth, death

example: some herbicides- 2,4-D, 2,4,5-T (components of agent orange)

Apical Dominance

Apical dominance is the inhibition of lateral buds by auxin from the apical bud.

Auxin is broken down as it moves down stem, so its concentration decreases.

lowest buds- least inhibited.

Removal of apical bud releases buds farther down

3.Cytokinins

- ❖ Stimulate cell division
- ❖ major source is the roots
- ✓ move upward (oppose auxin)
- ❖ Promote growth of lateral buds
- ✓ As plant grows, lower buds are more under the influence of cytokinins
- ❖ Prevents leaf senescence

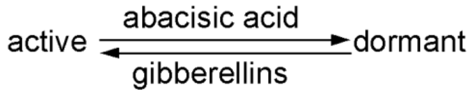
4.Ethylene

- ➢ Gas- dispersed by air
- ➢ produced by ripening fruits, accelerates ripening of nearby fruits
- ➢ stimulates senescence and abscission in leaves and fruits
- ✓ Abscission is apparently started by the relative decrease in auxin and perhaps gibberellin
- ✓ once started the process is stimulated by ethylene
- ➢ loosen cell wall
- ✓ Ethylene -released ***abscission layer*** - release of ***cellulose-*** digests cellulose , stretch. - cell wall is loosened.

5.Abscisic Acid (ABA)

- ● Stress hormone- protects plants
- ✓ Closes stomata (water shortage)- causes K^+ to leave guard cells

- Growth inhibitor- counteracts growth hormones
- accelerates abscission (dropping of leaves)
- moves only short distances from site of production
- induces and maintains dormancy (metabolic slowdown) in seeds and buds



✓ Some seeds will not germinate until the ABA is leached away.

6.3. Hormone Interactions

❖ Allows complex control of growth and development

- Auxin and cytokinin- the 2 major hormones used in culturing plant tissues.

✓ The ratio of auxin to cytokinin and the pH of the culture medium determine whether the plant tissue remains as an undifferentiated ***callus*** or differentiates to produce roots, vegetative shoots, leaves, or floral shoots

10. Hormones and nutrition biochemistry

10.1 Definition and general function

10.2 Classification of hormones and properties

10.3 Fat and water soluble vitamins

CHAPTER 11. Analytical biochemistry

11.1 Biochemical techniques

Analytical biochemistry

11.1 Biochemical techniques

Analytical chemistry seeks ever improved means of measuring the chemical composition of natural and artificial materials

The techniques of this science are used to identify the substances which may be present in a material and determine the exact amounts of the identified substances

<u>Qualitative:</u> *provides information about the identity of an atomic, molecular or biomolecular species*

<u>Quantitative:</u> *provides numerical information as to the relative amounts of species*